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PACKAGING

IV. METHODS OF APPLYING WATER-VAPOUR BARRIERS, AND THE WATER-VAPOUR RESISTANCE OF SOME PACKAGING MATERIALS[1]

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Abstract

Reynolds' Metal A–10 and 450 M.S.Y.T. "Cellophane" were used as liners and overwraps and Darex P–16 as a wax-dip for cartons containing sawdust, and packed in a master container. Some packages were dropped a distance of three feet, 20 times at −40° F., others received the same treatment at room temperature, and some were subjected to a free fall of about 70 ft. Greatest protection was provided by the use of a liner inside the carton.

Water-vapour resistance and ability to withstand rough handling were investigated for a wide variety of packaging materials (all materials but one tested as carton liners). Laminated materials having metal foil as one layer provided the greatest protection. Wax-coatings effectively reduced water-vapour transmission, but provided little added protection when packages were subjected to shock. Laminating two stocks produced marked reduction in the water-vapour transmission typical of either base sheet when used alone. Combinations utilizing scrim or kraft produced barriers that were less likely to fracture when subjected to rough handling. When Cellophane was considered, M.S.Y.T. stock and the use of triplex bags provided the greatest protection.

Introduction

The need for protection against loss or gain of water vapour by foods, particularly when frozen or dehydrated, is generally recognized in the food industry today. For this reason, a limited study of the water-vapour resistance of packaging materials has already been made in this laboratory (3). It was felt desirable to continue this work and evaluate thoroughly the effectiveness of the more important types of flexible barriers available in Canada.

During the course of preliminary studies (3), the question of the relative effectiveness of carton liners and overwraps was raised. In addition, no precise information was available to permit selection between the foregoing methods and wax-dipping as a means of providing protection against water-vapour penetration. Hence, prior to investigating individual materials an experiment was designed to evaluate the resistance to rough handling of packages made by these various methods.

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Relative Fragility of Water-vapour Barriers when Applied by Various Methods

Materials and Methods

The packaging materials selected for use in this portion of the investigation were: 450 M.S.Y.T. "Cellophane," Reynolds' Metal A–10 (a lamination of kraft to metal foil to Cellophane), and Darex Wax P–16 (a commercial dipping wax). These materials were used to prepare liners and overwraps or for wax-dipping 12 cartons, 4 by $2\frac{3}{4}$ by $1\frac{5}{16}$ in. (opening end $2\frac{3}{4}$ by $1\frac{5}{16}$ in.). These cartons were of the regular flat folding style with full overlapping long flaps and were made of 0.020 in. chipboard. The packages were filled with sawdust, closed, and packed in a master container which accommodated three layers each containing six by four or 24 upright packages. The master container was $12\frac{1}{4}$ by $11\frac{1}{8}$ by $12\frac{1}{4}$ in. high (opening end $12\frac{1}{4}$ by $11\frac{1}{8}$ in.), and was made of regular B-flute, utilizing $0.016 -0.009 -0.016$ Fourdrinier kraft liner and corrugations. Of 72 cartons in each master container, a set of 12 was under study and were packed in fixed positions (Fig. 1), the remaining space being filled with dummy packages containing sawdust.

Three experimental conditions of rough handling were investigated. The first involved cooling the packages to minus 40° F., and then dropping them 20 times through a distance of three feet to a cement floor (five falls on each of the four upright edges of the master container). The second treatment followed the same procedure at room temperature (approximately 75° F.). The third permitted a single fall of about 70 ft. on to cement (temperature of packages, approximately 75° F.). After treatment the packages were opened and the water-vapour barriers were examined visually for fractures, and for pin holes.

Results

The results of the visual examination of the packaging materials are given in Table I, and the data are summarized on a per cent basis in Table II. Of the materials used, Cellophane did not develop pin holes as easily as did Reynolds' Metal A–10, but it was more prone to fracture. Over-all, Cellophane appeared slightly more flexible than Reynolds' Metal, but this was not borne out by subsequent work, as will be shown later.

Reduction in temperature greatly increased the fragility of barriers when roughly handled. In addition, a number of short falls, a condition more likely to be met in ordinary commercial handling and transport, caused greater damage to the water-vapour barrier than a single fall from a much greater height.

Under the handling conditions described, wax-dipping was generally less desirable than either of the other two methods of providing water-vapour protection. While Darex P–16 may not be the most flexible wax obtainable,

TABLE I

FRAGILITY OF WATER-VAPOUR BARRIERS WHEN ROUGHLY HANDLED

Method of providing water-vapour barrier	Method of handling	Number of barriers		
		Unbroken	With pinholes	Fractured
Cartons with liners				
450 M.S.Y.T. Cellophane / Reynolds' Metal A–10	3 ft. drop, 20 falls at −40° F.	2 0	2 10	8 2
450 M.S.Y.T. Cellophane / Reynolds' Metal A–10	3 ft. drop, 20 falls at approx. 75° F.	7 3	2 9	3 0
450 M.S.Y.T. Cellophane / Reynolds' Metal A–10	70 ft. drop (approx.), one fall at approx. 75° F.	11 9	1 1	0 2
Overwrapped cartons				
450 M.S.Y.T. Cellophane / Reynolds' Metal A–10	3 ft. drop, 20 falls at −40° F.	0 0	0 2	12 10
450 M.S.Y.T. Cellophane / Reynolds' Metal A–10	3 ft. drop, 20 falls at approx. 75° F.	4 0	4 9	4 3
450 M.S.Y.T. Cellophane / Reynolds' Metal A–10	70 ft. drop (approx.), one fall at approx. 75° F.	8 6	1 3	3 3
Wax-dipped cartons				
Darex P–16	3 ft. drop, 20 falls at −40° F.	0	0	12
Darex P–16	3 ft. drop, 20 falls at approx 75° F.	0	0	12
Darex P–16	70 ft. drop (approx.), one fall at approx. 75° F.	0	0	12

the results are nevertheless indicative of what may be expected from this type of packaging using currently available waxes. It has been observed elsewhere (2) that rough handling caused an appreciable increase in the moisture gain of wax-dipped packages of dehydrated pork.

The most desirable method of providing water-vapour protection was a liner inside the carton (Table II). This method cannot be used, however, when the contents of the package are of such a nature as to effect possible rupture of the inner barrier. In such circumstances overwrapped cartons seemed to be more desirable. Subsequent work has shown, however, that the best method of packaging such materials is by the use of the container–barrier–container method (1). This consists of placing the product in a light carton, applying the water-vapour barrier, and placing the whole in another snugly fitting carton.

TABLE II

SUMMARY OF FACTORS AFFECTING THE FRAGILITY OF WATER-VAPOUR BARRIERS CONSIDERED OVER OTHER CONDITIONS

Factor	Per cent of barriers		
	Unbroken	With pinholes	Fractured
Method of providing barrier			
Liner	44	35	21
Overwrap	25	26	49
Wax-dip	0	0	100
Material			
Cellophane	44	14	42
Reynolds' Metal A–10	25	47	28
Darex P–16	0	0	100
*Method of handling**			
3 ft. drop, 20 falls at −40° F.	4	29	67
3 ft. drop, 20 falls at approx. 75° F.	29	50	21
70 ft. drop (approx.), single fall at approx. 75° F.	71	12	17

**Summary confined to liners and overwraps only.*

Water-vapour Transmission of Packaging Materials

Materials and Methods

Earlier work has indicated that the most satisfactory evaluation of the water-vapour resistance of packaging materials was obtained after fabrication into packages (3). Moreover, the experiment described above showed that the most desirable method of using a water-vapour barrier was as a liner inside the package. Hence, in the present work, all barriers (with one exception as noted below) were fabricated into carton liners.

The materials tested were different grades and plies of Cellophane, and various combinations of metal foil, scrim (a material similar to cheesecloth), kraft paper, glassine, Cellophane, Pliofilm, cellulose acetate, and vinylite. In addition, some of the materials were tested after waxing. Detailed descriptions of individual materials are given in Tables III, IV and V.

The materials were fabricated into pouch type liners, having outside dimensions of $5\frac{3}{8}$ by $6\frac{3}{4}$ in. high and inside dimensions of $4\frac{3}{8}$ by $6\frac{3}{4}$ in. high, suitable for use inside the chipboard carton which has already been described. The liners were opened, inserted into the cartons and partially filled with sawdust; then 73.5 gm. of anhydrous calcium chloride in a perforated P.T. Cellophane bag was added; this bag was surrounded by sawdust and the remainder of the liner was filled with sawdust. The liner and cartons were then sealed, sodium silicate glue being used to make the carton closure.

The one exception to the above procedure was the material composed of scrim laminated to M.S.A.T. Cellophane, both sides being waxed with micro-

crystalline wax. This material was designed for overwrapping, and so was applied in this way. A double fold was made at the side seam, and completed packages were dipped in microcrystalline wax held at 170° F.

Five tests were done on each packaging material, six completed packages being used for each test. Six packages without calcium chloride and sawdust were used as a means of estimating the sorption of water vapour by the packaging materials. To estimate the sorption by the material used as an overwrap, a set of dummy packages of the same size as the chipboard cartons used was made, using metal in place of the chipboard box, to eliminate all absorbent material beneath the barrier.

One set of six packages was placed in a cabinet operating at 95° F. and 100% relative humidity (high humidity cabinet, vapour-pressure differential approximately 42 mm. of mercury). Another set was placed in an alternating cabinet which operated at 80° F. and 100% relative humidity (vapour-pressure differential approximately 26 mm. of mercury) for 12 hr., and 120° F., 55% relative humidity (vapour-pressure differential approximately 48 mm. of mercury), for the remaining 12 hr. of the day. The latter test was designed to give packages an opportunity to breathe.

The remaining three sets of packages were subjected to various treatments before the water-vapour penetration was determined in the high humidity cabinet. One set was stored at 140° F. (relative humidity about 6%) for one month, to evaluate the effect on the barrier of storage under hot dry conditions. To simulate very severe conditions of handling and transport, one set was cooled to minus 40° F. and dropped three feet, 20 times (five falls on each upright edge of the master container). After cooling to minus 40° F. the remaining set was subjected to a vacuum of 20 in. of mercury for two hours, to reproduce conditions encountered in air transport. Dropping and low pressure tests were performed using a master carton, which has already been described. The arrangement of test packages in the master container is shown in Fig. 1. It will be noted that, in the dropping test, two of the packages were buried in the interior of the master carton, being surrounded by dummy packages, while the remaining four were placed at the edges of the master carton.

To determine moisture gain, packages, as individual units, were weighed before insertion in the cabinets and at weekly intervals for four weeks.

Since packages are not normally stored in an atmosphere of 95° F., 100% relative humidity, it was desirable to be able to interpret water-vapour transmission rates in terms of temperate room conditions. Hence, the transmission of three materials (Reynolds' Metal A–10, 300 M.S.A.T. Cellophane, and 300 M.S.T. Cellophane wax-coated 40 lb. per ream) was determined under the conditions existing in the laboratory, as well as in the high humidity cabinets. Packages were made up as previously described, and weighed at weekly intervals from August 1, 1945, to February 1, 1946.

Results

Water-vapour transmission rates are shown in Tables III, IV and V. To obtain these values, the weight of water vapour sorbed by the packaging materials (empty packages) at a given time was subtracted from the total increase in weight of the test packages, weighed at the same time. The slope

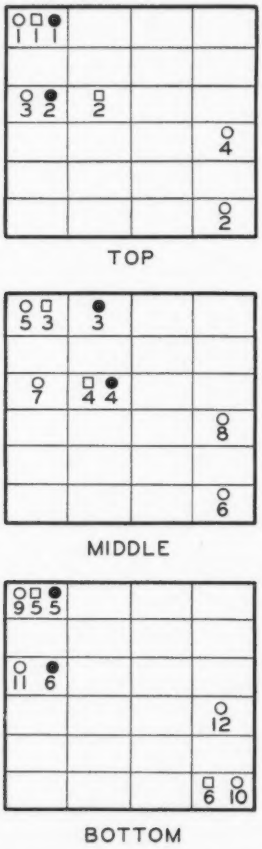

FIG. 1. *Packages in master container, arranged for handling trials (packages under study marked, all others dummies).*

○ *Dropping test, methods of application trials.*

● *Low pressure test.*

□ *Dropping test, material trials.*

of the line showing weight gain per week of the package contents over a period of one month was then calculated assuming a straight line relation.

The average standard error for the transmission rates, except those obtained after the dropping test, was 0.24, hence rates must differ by 0.48 gm. per

TABLE III

SUMMARY OF WEIGHT CHANGES IN PACKAGES UTILIZING CELLOPHANE AS A LINER

Material	Thicknesses	Seal	Sorption (gm.) by packaging materials held in high humidity cabinet	Water-vapour transmission (gm./week), high humidity cabinet; after treatments as follows:				Water-vapour transmission (gm./(week), alternating cabinet
				Untreated	One month at 140° F.	Subjection to low temp. and low pressure	Dropping* 20 times at −40° F.	
300 M.S.T.	Duplex	Crimp	1.84	0.89	10.78	1.66	6.82	1.44
300 M.S.A.T.	Duplex	Crimp	2.68	0.79	3.23	1.31	2.32	0.99
300 M.S.Y.T.	Duplex	Crimp	2.50	0.48	1.22	0.86	0.97	0.65
300 M.S.A.T.	Single	Crimp	1.44	1.46	8.83	2.75	4.92	1.30
300 M.S.A.T.	Duplex	Crimp	2.68	0.79	3.23	1.31	2.32	0.99
300 M.S.A.T.	Triplex	Crimp	3.37	0.25	0.62	0.82	2.17	0.78
300 M.S.A.T.	Duplex	Flat	2.96	0.31	5.50	0.96	2.87	0.83
300 M.S.A.T.	Duplex	Crimp	2.68	0.79	3.23	1.31	2.32	0.99

** Average for only two packages (see Table VI).*

week to be significantly different. As shown by Table VI, when most of the materials tested were subjected to dropping at −40° F., the four packages against the edges of the master container were fractured. For this reason, the water-vapour transmission rates obtained after the dropping were calculated from the gains of only the two packages buried in the interior of the master carton, and the standard error for these rates was larger, being 0.79. Keeping the above limits of accuracy in mind, it is possible to compare the protection offered by different materials under the conditions used.

Little difference was noted between the water-vapour transmission of untreated packages in the alternating and constant temperature cabinets, but any treatment simulating storage or transport markedly increased the rate of moisture gain (Tables III, IV, and V). After subjection to low temperature and pressure, the majority of packages showed a substantial increase in water-vapour penetration; however, the increase was no greater than that caused by the other handling tests, and no fractures in packaging material resulted from this treatment. This indicates that air transport should not damage packages extensively, provided air volumes inside the barriers are kept to a minimum.

When Cellophane was considered, it was apparent that M.S.Y.T. stock provided greater protection than M.S.A.T., which in turn was better than M.S.T. (Table III). The use of triplex bags gave maximum resistance to water vapour. A flat seal appeared to be generally more desirable than a crimp seal, although the latter was superior for excessively high storage temperatures.

TABLE IV

SUMMARY OF WEIGHT CHANGES IN PACKAGES USING PLAIN OR WAX-COATED MATERIALS AS LINERS

Stock	Processing	Heat sealed	Sorption (gm.) by packaging materials held in high humidity cabinet	Water-vapour transmission (gm./week), high humidity cabinet: after treatment as follows:				Water-vapour transmission (gm./week), alternating cabinet
				Untreated	One month at 140° F.	Subjection to low temp. and low press.	Dropping* 20 times at −40° F.	
40 lb. kraft	Wax-impregnated	(Adhesive sealed)	3.38	14.0‡	7.32‡	13.2‡	17.8‡	6.16
40 lb. wet strength kraft	Wax-coated†† 40 lb./ream	Flat	7.58	1.42	1.77	1.86	3.79	2.83
25 lb. bleached glassine	Thermoplastic coated one side	Flat	1.94	4.97	†	6.98	15.66	4.61
25 lb. bleached glassine	Wax-coated†† 40 lb./ream	Flat	8.46	0.84§	1.19	1.25§	†	2.06
300 M.S.T. Cellophane	None	Flat	2.28	1.85	33.0‡	2.41	10.06	1.50
300 M.S.T. Cellophane	Wax-coated†† 40 lb./ream	Flat	8.50	0.79	0.31	3.02	†	0.80
Laminated 300 M.S.T. Cellophane	None	Flat	4.10	0.59	0.08	0.46§	1.76	0.66
Laminated 300 M.S.T. Cellophane	Wax-coated†† 40 lb./ream	Flat	3.57	0.24	0.06	0.08	0.89	0.04
Pliofilm	None	Flat	1.43	1.18	1.27	1.35	2.03	1.16
Scrim laminated to M.S.A.T. Cellophane waxed both sides	Applied as overwrap. Package wax-dipped.							
	(*a*) Scrim side in	—	0.18	0.17	0.39	0.13	0.19	0.11
	(*b*) Scrim side out	—	0.75	0.02	0.22	0.39	0.17	0.14

* *Average for only two packages (See Table VI).*

† *Complete failure under these conditions.*

‡ *Measurement for first two weeks only, complete failure.*

§ *Averages for five packages only—one failure under these conditions.*

†† *Flexible wax composition.*

Wax-coating (40 lb. per ream) various base stocks reduced the moisture penetration to less than one-half; but the transmission of all stocks was not reduced to a common value, i.e., the more dense the base stock the lower the water-vapour transmission after waxing (Table IV). Wax-coating Cellophane and glassine reduced the moisture gain after ageing at 140° F., but did little to increase resistance to fracture at low temperature (Tables IV and VI). It will be noted that the material that was applied as an overwrap withstood dropping slightly better than other waxed materials. This was due to the fact that the wax on this material was more flexible than that on the coated materials, and

to the strength imparted to it by the scrim incorporated into the sheet. It must be borne in mind, however, that the transmissions reported after drop-

TABLE V

SUMMARY OF WEIGHT CHANGES IN PACKAGES USING LAMINATED MATERIALS AS LINERS

Stock	Laminated to: (wax laminated unless otherwise stated)	Heat sealed	Sorption (gm.) by packaging materials held in high humidity cabinet	Water-vapour transmission, (gm./week), high humidity cabinet; after treatment as follows:				Water-vapour transmission, (gm./week), alternating cabinet
				Untreated	One month at 140° F.	Subjection to low temp. and low press.	Dropping* 20 times at −40° F.	
Scrim (Reynolds' A–50)	Kraft and alloyed lead foil with butvar coating (asphalt lam.)	Flat and reinforced with cellulose tape	1.79	0.02	0.25	0.00	0.60	0.04
25 lb. kraft	25 lb. kraft, thermoplastic coated one side	Flat	2.04	8.92	29.26†	17.96†	15.55†	4.92
25 lb. kraft	25 lb. glassine, thermoplastic coated on glassine	Flat	2.40	2.36	10.90‡	2.64	3.63	3.77††
White kraft	300 M.S.T. Cellophane	Crimp	3.92	0.80	0.46	1.13	5.48	0.43
25 lb. kraft	300 M.S.A.T. Cellophane	Flat	3.50	0.80	1.30	1.40	2.83	0.79
25 lb. kraft	Cellulose acetate, thermoplastic coated on acetate side	Flat	2.24	1.62	9.73	4.78	6.58	1.42
25 lb. kraft (Reynolds' A–15)	Alloyed lead foil, (asphalt lam.), thermoplastic coat on foil	Flat	0.85	0.24	0.30	0.34	1.20	0.22
40 lb. kraft (Reynolds' A–10)	Alloyed lead foil and Cellophane (asphalt lam.)	Flat	2.15	0.00	0.13	0.10	0.97	0.13
25 lb. glassine	25 lb. glassine, thermoplastic coated one side	Flat	2.08	1.24	1.14	1.59	1.92	3.78
25 lb. glassine	300 M.S.T. Cellophane	Crimp	1.03	0.77	0.24	0.99	4.95	0.49
300 M.S.T. Cellophane	300 M.S.T. Cellophane	Flat	4.10	0.59	0.08	0.46§	1.76	0.66
300 M.S.T. Cellophane	Aluminum foil	Crimp	1.43	0.05	0.37	0.35	1.43	0.19
Vinylite	Both sides of aluminum foil	Flat	2.06	0.00	0.00	0.00	0.00	0.00

* *Average for only two packages (See Table VI).*

† *Complete failure under these conditions.*

‡ *Measurements for first three weeks only, complete failure.*

§ *Average for five packages only, one failure under the conditions.*

†† *Average for four packages only, two failures under these conditions.*

TABLE VI

ABILITY OF PACKAGES TO WITHSTAND 20 DROPS OF THREE FEET EACH AT −40° F. (−40° C.)

Stock	Processing	Packages unbroken—* (six tested)	Packages with water-vapour transmission comparable to that of interior packages
Scrim (Reynolds' A–50)	Laminated to kraft and foil with butvar coating	6	4
40 lb. kraft	Wax-impregnated	6	0
White kraft	Laminated to 300 M.S.T. Cellophane	6	1
Metal foil	Laminated to 300 M.S.T. Cellophane	6	0
Scrim laminated to M.S.A.T. Cellophane waxed both sides	Applied as overwrap. Package wax dipped. (*a*) Scrim side in	6	1
	(*b*) Scrim side out	6	0
Kraft (Reynolds' A–10)	Laminated to metal foil and Cellophane	5	0
25 lb. kraft (Reynolds' A–15)	Laminated to metal foil with thermoplastic coating	5	0
25 lb. kraft	Laminated to cellulose acetate	5	1
Vinylite	Laminated to both sides of aluminum foil	4	2
40 lb. kraft (wet strength)	Wax-coated 40 lb./ream	3	0
25 lb. kraft	Laminated to 25 lb. glassine	3	0
25 lb. kraft	Laminated to 300 M.S.A.T. Cellophane	3	0
300 M.S.T. Cellophane	Laminated to 300 M.S.T. Cellophane	3	1

* *All other types had only two interior packages unbroken (see Tables III, IV, and V).*

ping were based on the two interior packages only, and must be considered in conjunction with Table VI.

Laminated materials having metal foil as one layer provided greater protection than any other materials (Table V). The results also show that laminating two stocks produced marked reduction in the water-vapour transmission typical of either base sheet when used alone. The lamination of vinylite to metal foil illustrates that it is possible to produce a very water-vapour resistant package by combining a material that is not water-vapour resistant with one that is. Vinylite is not considered water-vapour proof and was utilized in this combination to provide strength and heat sealing properties.

Table VI shows the number of packages remaining unfractured after the dropping test, and indicates that the great majority of materials tested require protection from such treatment. Laminations utilizing scrim or kraft were less likely to fracture when roughly handled, but absence of a visible break did not necessarily mean that the water-vapour transmission rate had not increased considerably.

Under room conditions, the water-vapour transmission rates of Reynolds' Metal A–10, 300 M.S.A.T. Cellophane, and 300 M.S.T. Cellophane wax-coated 40 lb. per ream were 0.00, 0.20, and 0.11 gm. per week, respectively. The foil barrier had an undetectable transmission rate in the high humidity cabinet (untreated packages, Table V), and this was also true under room conditions. However, for 300 M.S.A.T. Cellophane and for wax-coated Cellophane, the ratio of the water-vapour transmission in the high humidity cabinet to the transmission under room conditions was 7.3 and 7.2, respectively.

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DRIED WHOLE EGG POWDER

XXII. SOME FACTORS AFFECTING THE PRODUCTION AND INITIAL QUALITY OF DRIED SUGAR-AND-EGG MIXTURES[1]

By Jesse A. Pearce[2], J. Brooks[3], and H. Tessier[4]

Abstract

Sugar–egg powder was produced under a variety of conditions in a laboratory spray drier and in two commercial driers. A product prepared at inlet temperatures below 270° F. and outlet temperatures below 150° F. was the most suitable for baking purposes and was generally the best when assessed by measurements of fluorescence, potassium chloride value, and pH. Powder of particle size small enough to pass an 80 mesh screen (U.S. Bureau of Standards) appeared to have better baking properties than coarser material. Trials with nozzles of various sizes indicated that the best product was prepared using small nozzles. Sucrose syrup or solid sucrose, with fresh or frozen egg, all produced powders of similar initial quality.

Introduction

The addition of sucrose sugar to liquid egg before drying is known to provide protection during heat treatment (2) and storage of the dried product (1, 3). The product is much more suitable than plain egg powder for use in baked goods (2). However, no information was available about the best conditions for producing this material. Since it is expected that Canada will produce about $20\frac{1}{4}$ million pounds of dried sugar–egg powder during 1946, it was believed desirable to examine certain factors in the processing procedure that may affect the quality.

Materials and Methods

The liquid from fresh, Grade *A*, shell eggs, except as noted in Fig. 1, was used in operations on the laboratory cone-type drier (11), while liquid from frozen egg was used for all work on two commercial cone-type driers, except as noted in Table II.

Rate of production at specific drying conditions for some of the work done in the commercial plants is given in Table I. The effect of air temperature and nozzle diameter on the rate of powder production can be estimated from Table I and the data in the other tables and Fig. 1.

The quality of the powder was determined by measurement of the moisture content (9), fluorescence value (5), potassium chloride value (9), pH (4), baking volume (6), foaming volume (6), and foam stability. In addition,

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TABLE I

DRYING CONDITIONS AND RATE OF SUGAR–EGG PRODUCTION FOR SOME OF THE WORK DONE IN THE COMMERCIAL PLANTS

Plant	Inlet temperature, ° F.	Outlet temperature, ° F.	Nozzle diameter, in.	Pump pressure, p.s.i.	Production, lb./hr.
1	285	155	0.0635	4300	700
2*	240	155	0.0700	4400	700

* *Uses preheater on egg just before it goes to spray nozzle in drier.*

some samples were subjected to a sieve analysis to obtain fractions of different particle sizes. The procedures for determining baking volume and foaming volume were unsatisfactory and were modified as noted below.

To prepare sponge cakes for the determination of baking volume, all the materials used were brought to a temperature of 80° F. and all mixing was done in a room at 80° F. and 65% relative humidity. The procedure was as follows.

Sugar–egg powder (9 gm.) was mixed, by hand, with 17 gm. of commercial, powdered sugar (sucrose) in the small bowl of a Mixmaster. A portion of a measured volume of 19 ml. of tap water was added and mixed into a paste with the sugar and powder. The remainder of the water was added and mixed with the paste until a homogeneous liquid was obtained. The beaters of the Mixmaster were then lowered into the bowl so they just touched the bottom and were allowed to whip the mixture for 10 min. while operating at No. 10 speed. After five minutes' beating, the bowl was turned by hand through 90°, but no other motion of the bowl was permitted. Small portions of a 20 gm. quantity of a standardized super-cake flour were sprinkled over the surface and each portion was carefully mixed in with a rubber spatula in such a manner that the foam was disturbed as little as possible. The batter was then carefully scraped from the beaters and bowl and transferred to an ungreased pan, which was immediately inserted into an oven (400° F.) and baked for 15 min. After baking, the sponge and pan were inverted and allowed to stand in the conditioned room overnight. The next day, the volume of the cake was measured. The standard deviation of this volume-measuring technique was 2.4 ml.

It was observed that two different technicians produced cakes with an average difference in volume of 12 ml., therefore, most of the baking was done by one person only. For this person, three cakes were necessary to show a significant difference of 10 ml. in the baking volume of the powders. Therefore, all values shown are the average of volume measurements on three cakes. No significant day-to-day differences in cake volume were observed.

To determine foaming volume the requirements for conditioning and mixing the materials were the same as for the baking test. Otherwise, the

quantities of material and the procedure described elsewhere were used (2). Foam stability was evaluated by inverting the graduate cylinder, in which foaming volume was measured. The time required for the foam to begin dripping from the cylinder was determined.

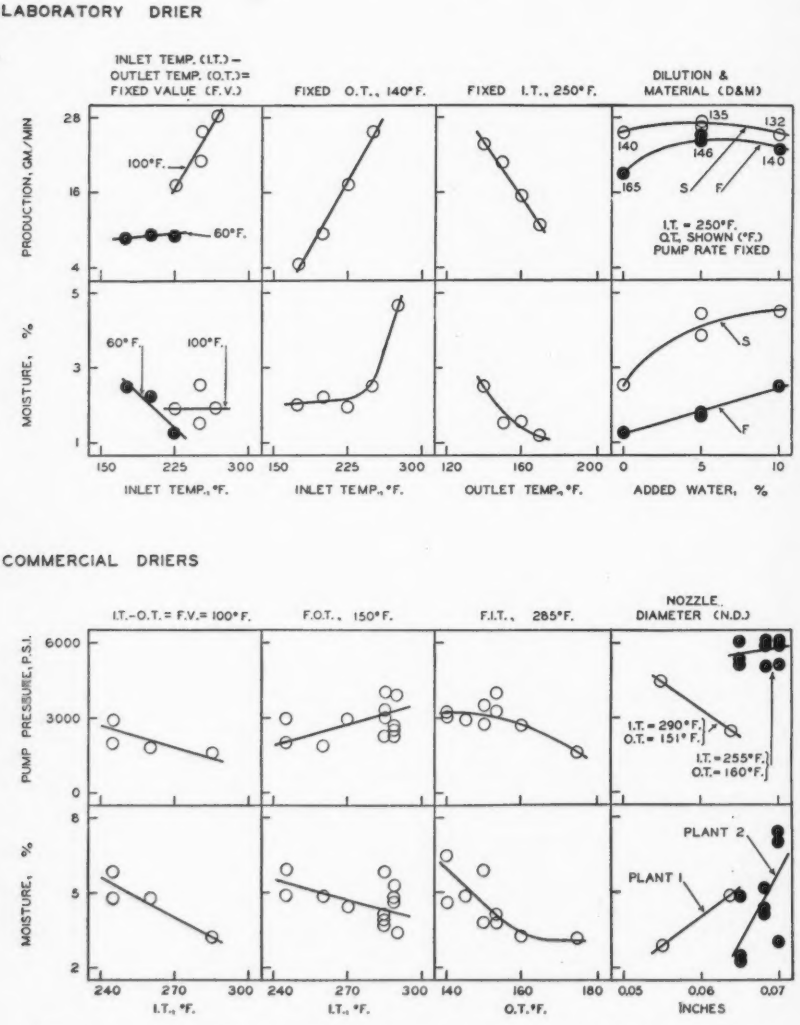

FIG. 1. *The effect of drying conditions on the moisture content and rate of production (shown as pump pressures in commercial driers) of sugar-egg powder.*

Laboratory drier: ○, *powder from fresh shell eggs (S);* ●, *powder from frozen liquid eggs (F).*

Commercial drier: ○, *operations at Plant 1;* ●, *operations at Plant 2.*

Particle size separations were done using screens of 16, 35, 65, 100, 200, and 325 mesh (U.S. Bureau of Standards). Previous examination indicated that one hour on a Ro-tap shaker was the most desirable sieving time, and this sieving period was used throughout. However, it has since become apparent that even this time did not provide complete separation of particles of different size (8).

Results

Laboratory Drier

The use of low drying temperatures reduced the rate of production and resulted in increased moisture content in the powder (Fig. 1); this corroborated the results of a previous study on plain egg powder (10). However, powder produced at an inlet temperature of 280° F. and an outlet temperature of 140° F. had an unexpectedly high moisture content. This may be attributable to the low volume of air passing through this drier and the high liquid flow rates necessary to maintain the low outlet temperature. Under these conditions, adequate removal of the water vapour was not possible.

As with plain egg powder (10), the present work showed that the best product, as assessed by all quality measures, was produced at the lowest temperatures (Fig. 2). One anomalous result was noted in the studies using fixed outlet temperatures. Materials produced at an outlet temperature of 150° F. had lower fluorescence values than material produced at 140° or 160° F. These products also had higher foaming volumes than material produced at 140° F. In general, the results indicated that, for this drier, good quality sugar–egg powder could be produced at an inlet temperature of 270° F. and that outlet temperatures of about 140° to 150° F. were satisfactory.

For a fixed pump rate a smaller amount of powder was produced from frozen melange than from fresh liquid egg (Fig. 1). This was attributable to the greater viscosity characteristic of stored, frozen, liquid egg. (It is possible that this high viscosity might be reduced by the addition of sugar to the liquid egg before freezing.) The moisture content was lower owing to the higher outlet temperatures associated with the lower throughput. However, by appropriate dilution, it was possible to prepare material from frozen melange that was similar in quality to that prepared from fresh eggs. As might be expected, at a fixed pump rate, dilution reduced the outlet temperature, with a corresponding increase in powder quality and moisture content.

Several additional factors were examined using the laboratory drier (Table II). These results showed that no significant difference resulted from the use of solid sugar or sucrose syrup, or from the sugars currently available in Canada and likely to be used by the various producers. Rapid beating of the sugar and liquid egg before drying increased the fluorescence value and decreased the potassium chloride value although it had no significant effect on baking quality.

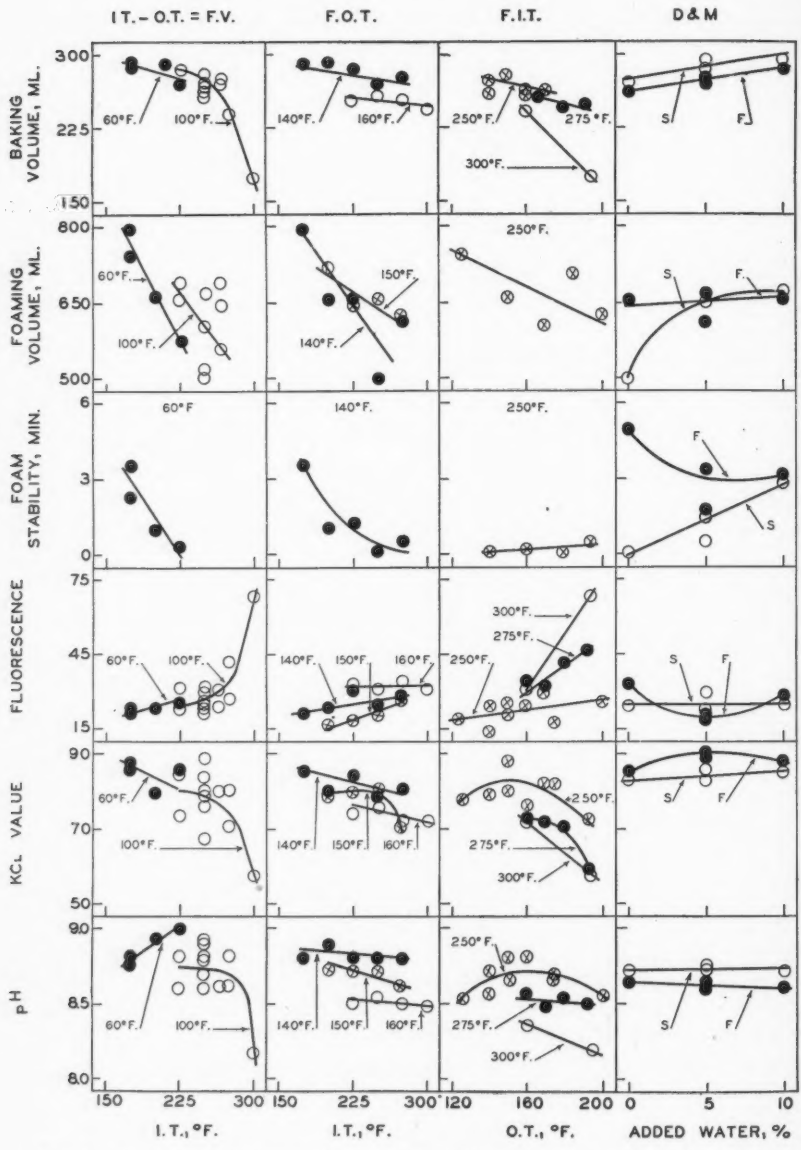

FIG. 2. *The effect of drying conditions on the quality of sugar–egg powder produced on laboratory drier (for abbreviations, see Fig. 1):* ○, *powder from fresh shell eggs (S);* ●, *powder from frozen liquid eggs (F). The average baking volume for sponges prepared from shell eggs was 286 ml.*

TABLE II

EFFECT OF MISCELLANEOUS ITEMS ON POWDER PRODUCTION AND POWDER QUALITY—LABORATORY DRIER

Item	Number of trials	Inlet temp., °F.	Outlet temp., °F.	Powder production, gm./min.	Powder quality						
					Moisture, %	Baking volume, ml.	Foaming volume, ml.	Foam stability, min.	Fluorescence value	Potassium chloride value	pH
Sugar vs. syrup (about 55% sucrose)											
Set 1											
Sugar	9	250	150	18.8	2.8	—	662	—	22.1	76.7	8.6
Syrup	9	250	150	14.2	4.0	—	682	—	21.1	78.6	8.6
Set 2											
Sugar	3	225	160	—	—	273	—	—	34.8	78.8	8.7
Syrup	3	225	160	—	—	265	—	—	34.6	77.1	8.5
Effect of sugar from different areas											
Alta. (beet)	3	250	140	—	—	284	670	2.5	17.7	81.2	8.8
Man. (beet)	3	250	140	—	—	286	687	2.5	18.3	83.5	8.8
Ont. (cane)	3	250	140	—	—	286	710	4.0	18.2	81.1	8.8
Effect of rate of stirring egg and sugar before drying											
Fast (causes foaming)	2	250	140	25.8	2.78	280	633	1.5	26.1	84.8	8.8
Slow (no foaming)	2	250	140	25.8	3.05	276	656	1.9	21.8	88.0	8.6

Commercial Driers

For the commercial driers, as for the laboratory drier, it was apparent that reduction in the inlet temperature, with a fixed outlet temperature, decreased production (estimated from pump pressure changes noted in Fig. 1) and resulted in a product with increased moisture content. Reducing the diameter of the spray nozzle lowered the moisture content, but did not affect production if the pump pressure was increased.

By all quality criteria, except foam stability and pH, the best product was produced at the lowest drying temperatures (Fig. 3). The foam stability measurement gave irregular results but this measurement was believed to be of less importance than baking volume. No explanation can be offered for the exceptionally high pH values observed for material produced at inlet temperatures higher than 285° F. for Plant 1 and 280° F. for Plant 2. In general, inlet temperatures of 270° F. and lower were most satisfactory. For Plant 1, an outlet temperature of 150° F. or lower was most desirable. Because of

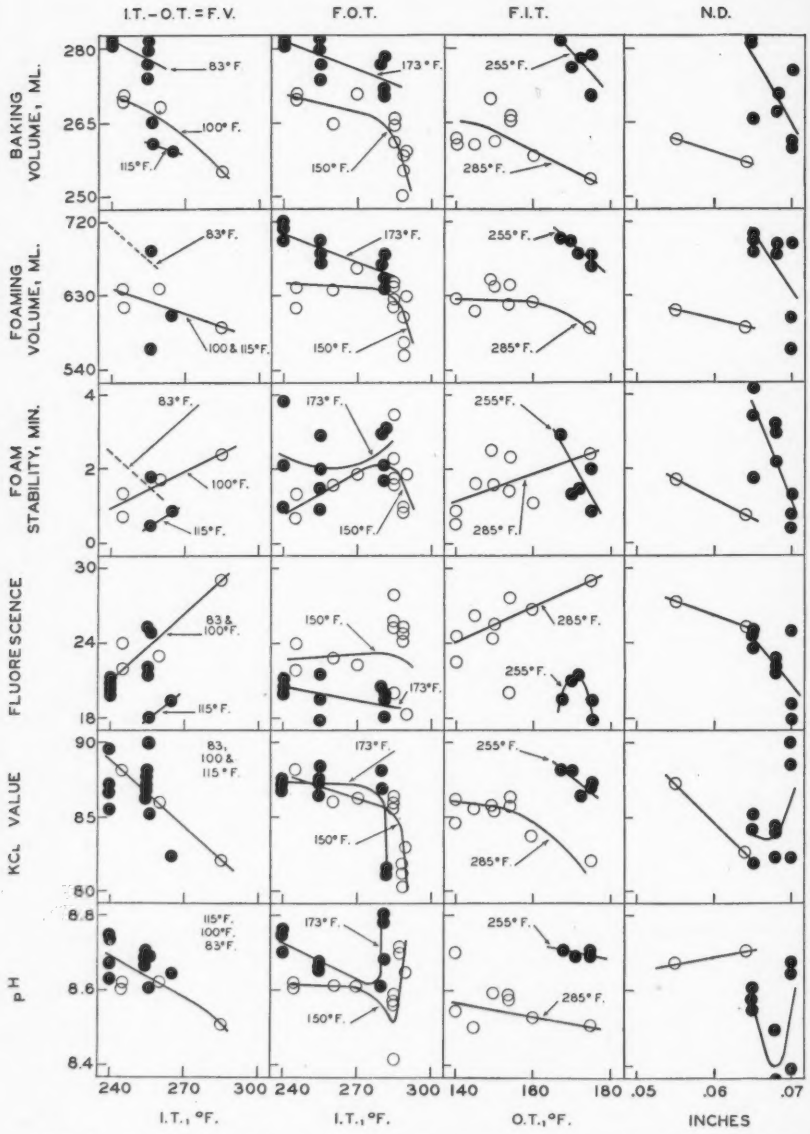

FIG. 3. *The effect of drying conditions on the quality of sugar-egg powder produced on commercial driers (for abbreviations, see Fig. 1): ○, operations at Plant 1; ●, operations at Plant 2; dotted lines, trials at Plant 2, points omitted to avoid confusion. All studies shown in the first three columns done at nozzle diameters of 0.064 in. and 0.070 in Plants 1 and 2, respectively. The average baking volume for sponges prepared from shell eggs was 286 ml.*

the limited range studied it was difficult to evaluate the most desirable outlet temperatures for Plant 2, but, again, the indications were that the lowest temperatures were the most desirable.

The size of the spray nozzle used was important. Results from both plants showed that the smaller the nozzle diameter the better the baking quality of the product and the lower the moisture content of the powder, but the fluorescence values were slightly increased. Nevertheless, the powders produced would meet the requirements of the tentative specification for Grade *A* sugar–egg powder (7). Further trials in Plant 2, using a multiple nozzle (three openings, 0.055 in.), gave products with baking volumes of 289 and 291 ml.

Baking tests were also done on fractions sieved from the various powders (Table III). These results supported the foregoing evidence and indicated that, for best baking quality, the powder should be fine enough to pass an 80 mesh screen.

TABLE III

THE EFFECT OF PARTICLE SIZE ON THE BAKING QUALITY OF SUGAR–EGG POWDER

Baking volume of whole sample, ml.	Baking volume (ml.) of sieved portions falling between the following sieve sizes (U.S. Bureau of Standards):					
	16-35	35-65	65-80	80-100	100-200	200-325
283	—	—	262	273	279	—
282	—	—	—	—	276	279
269	—	274	282	—	272	—
266	—	267	—	264	272	—
266	—	275	265	—	257	—
265	—	259	254	—	265	—
265	—	228	250	—	252	254
264	—	268	272	—	271	—
259	—	268	261	275	269	—
259	248	254	256	—	257	—
Average	248	262	263	271	263	266

Several additional factors were examined (Table IV). The increased temperature difference necessary when producing powder in wet weather caused a slight increase in fluorescence value and a slight decrease in potassium chloride and foaming volume values. The temperature of the powder at the time of packing had no significant effect on the baking quality of the product. Differences in powders produced from diluted liquid egg (fresh, shell), mixtures of frozen and shell egg liquids, and frozen egg were not significant. Powders of similar quality were produced by the addition of sugar in either solid or liquid form.

Discussion

The results obtained using either the laboratory or commercial driers showed that sugar–egg powder with excellent baking properties can be produced at inlet temperatures of 270° F. or lower and at outlet temperatures

TABLE IV

EFFECT OF MISCELLANEOUS ITEMS ON POWDER PRODUCTION AND POWDER QUALITY—COMMERCIAL DRIERS

Item	Number of trials	Inlet temp., °F.	Outlet temp., °F.	Powder production, gm./min.	Powder quality						
					Moisture, %	Baking volume, ml.	Foaming volume, ml.	Foam stability, min.	Fluorescence value	Potassium chloride value	pH
Dry weather	9	285	255	3244	3.92	262	632	2.2	22.7	86.2	8.6
Wet weather	8	290	250	3098	4.67	260	593	1.2	24.1	84.3	8.6
Powder packaged at average temperature of 78° F.											
Plant 1	2	289	152	3170	4.05	254	610	1.4	21.7	83.6	8.7
Plant 2	1	255	162	6000	4.12	267	695	3.0	21.6	84.1	8.4
Average					4.07	258	638	1.9	21.7	83.8	8.6
Powder packaged at average temperature of 106° F.											
Plant 1	2	288	151	2400	5.23	256	564	1.0	24.5	82.5	8.7
Plant 2	1	255	162	6000	4.33	270	685	3.5	22.9	84.8	8.2
Average					4.93	261	604	1.8	24.0	83.3	8.5
Frozen vs. fresh shell liquid, and dilution											
Shell (undiluted)	3	285	152	3300	3.22	260	627	2.0	21.4	86.8	8.6
Shell plus 7% water	1	285	154	3300	3.81	260	617	2.5	25.8	87.2	8.6
1 part shell and 3 parts frozen	1	285	153	3000	4.01	264	628	3.5	25.5	86.2	8.4
Frozen plus 7% water	4	285	154	3680	3.86	266	616	2.0	23.0	86.8	8.6
Sugar vs. syrup (about 55% sucrose)											
Plant 1											
Sugar	3	285	154	3350	4.02	265	640	2.3	20.2	86.8	8.6
Syrup	3	285	155	3300	3.76	257	611	2.2	22.7	86.0	8.6
Plant 2											
Sugar	1	257	155	6000	4.94	266	685	1.8	24.9	85.2	8.6
Syrup	1	255	160	5300	2.52	283	688	3.4	25.0	83.8	8.6

of 150° F. or lower. These conditions permitted fairly rapid production and, when small nozzles were used, produced powder with less than 3.0% moisture (2). It is also of interest to note that in the commercial trials the plant using a preheater for the liquid egg produced powder with better baking quality.

The present results showed that no improvement in initial baking quality resulted from cooling the product before packaging. Heat treatment studies have shown that rapid cooling of the product on removal from the drier is an essential (2).

Although the average value obtained for the baking volume of cakes from shell eggs of varying quality was 286 ml. (range 266 to 305 ml.), powder prepared on the laboratory drier produced cakes with baking volumes as high as 300 ml. This was attributed in part to the use of fresh shell eggs in this drier, but the major factor believed responsible was the use of an extremely small nozzle (0.025 in.).

While this study showed little difference in the initial quality of products prepared using solid sugar or sucrose syrup and using fresh eggs and frozen melange, it has been observed elsewhere that the use of syrup and the use of frozen melange resulted in products that were less stable when stored (2). In addition, the use of syrup necessitates the removal of a greater quantity of water, thereby increasing the cost of production.

Acknowledgments

The authors wish to express their thanks to members of the Special Products Board, Dominion Department of Agriculture, and to the companies concerned for their very kind co-operation.

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DRIED WHOLE EGG POWDER

XXIII. THE EFFECT OF MOISTURE CONTENT AND METHOD OF PACKING ON THE STORAGE LIFE OF DRIED SUGAR-EGG MIXTURES[1]

By R. L. Hay[2] and Jesse A. Pearce[2]

Abstract

Dried sugar–egg powders, obtained from a commercial Canadian source, were adjusted to 1.4, 2.8, and 3.2% moisture and stored at 40°, 80°, and 120° F. from 1 to 52 weeks. Quality of the powder was assessed by measurement of fluorescence, potassium chloride value, pH, and foaming volume. The rate of deterioration increased with an increase in moisture content at 80° and 120° F. The effect of moisture content on fluorescence and potassium chloride values was negligible at 40° F., but high moisture in powders stored at this temperature accelerated the development of acidity and the loss in baking quality as assessed by foaming volume.

Packing in carbon dioxide, nitrogen, and *in vacuo* had a slight beneficial effect on dried sugar–egg powder.

Introduction

Lowering the moisture and volatile content of plain egg powder to 2% has been found to exert a definite beneficial effect on storage life (10). Moisture levels of less than 1% improved the keeping qualities of dried albumen and whole egg but not of dried yolk (7). In a recent investigation, sugar–egg powder tempered to a 1.4% moisture level was considerably better than a similar powder with a 2.8% moisture content, when held at elevated temperatures (1). Packing in carbon dioxide had a definite preservative action on stored plain egg powder but packing in nitrogen and under vacuum had no beneficial effect (9, 11).

The present paper deals with the effects of low moisture content and of packing with carbon dioxide, nitrogen, and *in vacuo* (inert packs) on the keeping quality of sugar–egg powder stored for one year.

Materials and Methods

The sugar–egg powder (33% sugar, dry basis) used in this investigation was similar to that described in an earlier paper (1) and was adjusted to moisture levels of 1.4, 2.8, and 3.2%. Samples at all moisture levels were sealed in an atmosphere of air: samples at 2.8% moisture were also sealed in carbon dioxide, nitrogen, and under vacuum. All were examined after storage for one, two, and four weeks at 120° F.; after 1, 2, 4, 8, 16, and 32 weeks at 80° F.; and after 16, 32, and 52 weeks at 40° F. The quality of the egg powder was assessed by measurement of fluorescence (4), potassium chloride value (8), pH (8), and foaming volume (1, 5).

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During this investigation, it was observed that the foaming volume test was not entirely satisfactory, and, as a result, a baking test has been substituted in other work in these laboratories (2). While foaming volume has proved inferior to the baking test, the former can be utilized to evaulate the baking quality of sugar–egg powder, when comparing powders from the same source.

Results

The results are presented in Figs. 1 to 4. It should be noted that the time intervals are shown as a geometrical progression, to permit graphical comparison of changes at high and low storage temperatures.

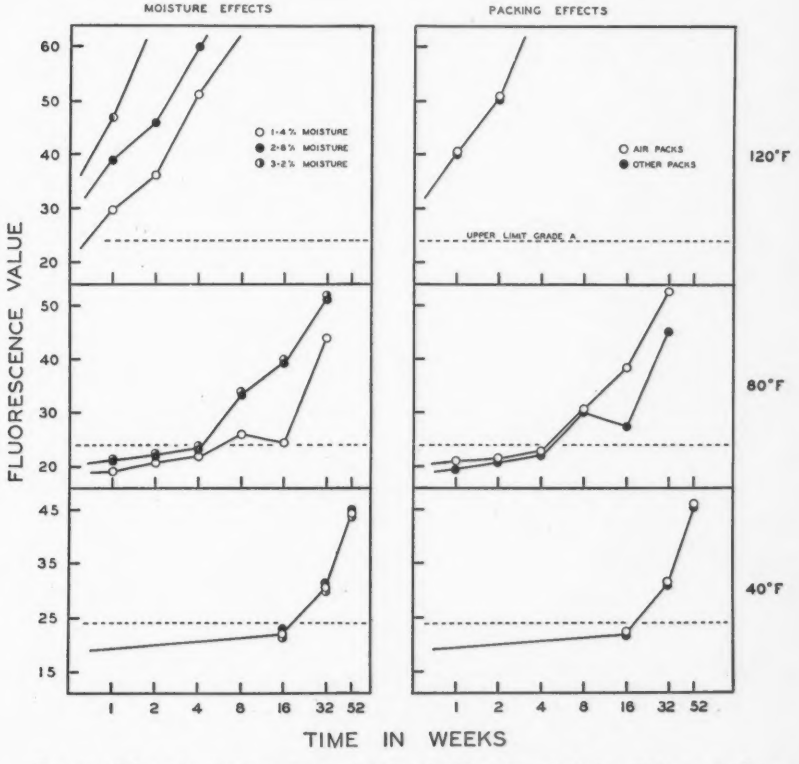

FIG. 1. *Effect of moisture contents of 1.4 to 3.2% and method of packing on the fluorescence values of dried sugar–egg powders.*

The Effect of Moisture Content

An increase in moisture content in the powder resulted in accelerated fluorescence development at 80° and 120° F. but had no measurable effect on the fluorescence of powders stored at 40° F. (Fig. 1). At 40° F. fluorescence

changes in the powders at all three moisture levels were negligible during the first 16 weeks, but fluorescence increased considerably and at equal rates for all moisture levels during the subsequent portion of the storage period. At 80° F. the fluorescence values of all powders increased slowly and at equal rates during the first four weeks, but subsequent changes in the 2.8 and 3.2% powders were much more rapid than in the 1.4% egg powder. At this temperature, reducing the moisture content from 2.8 to 1.4% appeared to

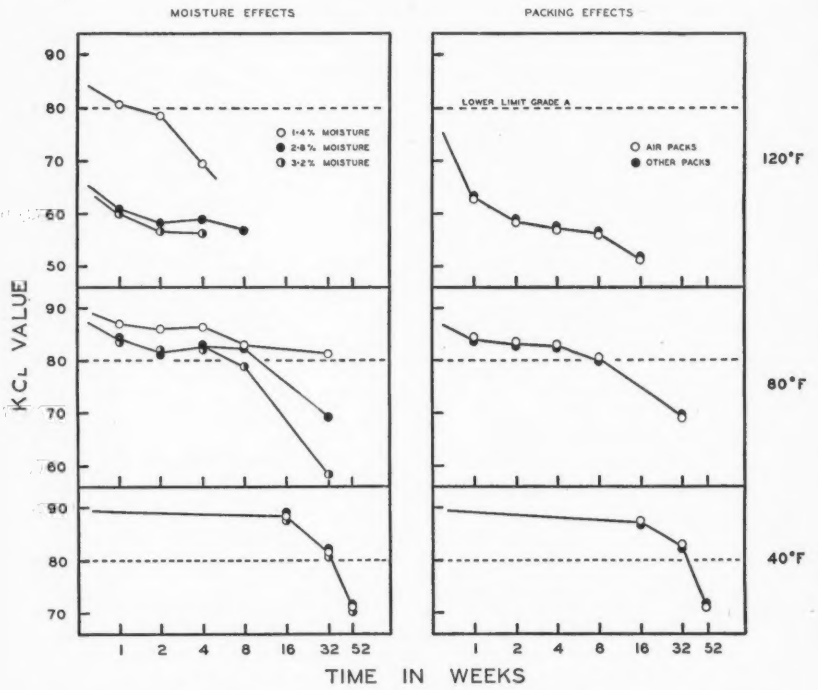

FIG. 2. *Effect of moisture contents of 1.4 to 3.2% and method of packing on the potassium chloride values of dried sugar–egg powders.*

increase the storage life of sugar–egg powder by about 12 weeks. The difference in behaviour between the several moisture levels was most marked at 120° F., the 1.4% powder remaining at the lowest fluorescence level during the entire storage period.

The behaviour of the potassium chloride values in this study (Fig. 2) agreed with and supported the results noted above for the fluorescence test. Lowering the moisture content from 3.2 to 1.4% did not appear to prolong the storage life of sugar–egg powder when stored at 40° F. for one year. However, at both 80° and 120° F. the beneficial effects of reduction in moisture content from 3.2 to 1.4% were quite marked. At 80° F. loss in quality of the 1.4%

powder was comparatively small. The 3.2% samples deteriorated at approximately the same rate as those containing 2.8% moisture during the first four weeks of storage at 80° F., but showed a more rapid loss in solubility during the remaining portion of the storage period. Changes in potassium chloride value were rapid in all powders stored at 120° F., the most marked occurring in the 2.8 and 3.2% powders during the first week.

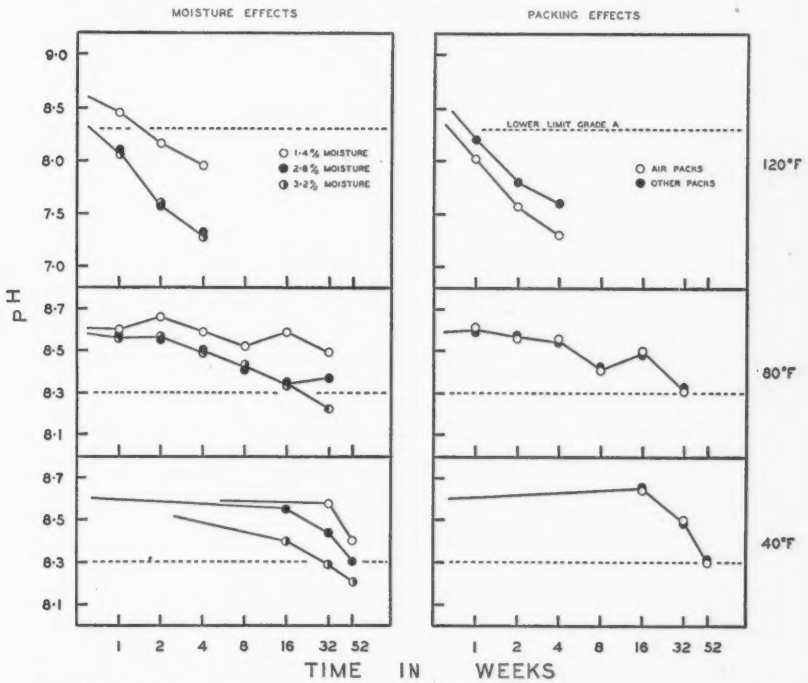

FIG. 3. *Effect of moisture contents of 1.4 to 3.2% and method of packing on the pH values of dried sugar–egg powders.*

The pH measurements (Fig. 3) gave further evidence that very low moisture contents are advantageous. At all temperatures studied, powders containing 1.4% moisture maintained a higher pH level than either the 2.8 or 3.2% powders. There was little difference between the 2.8 and 3.2% powders at the higher temperatures, but, unlike the other tests, this test showed that reduced moisture content prolonged storage life at 40° F.

Notwithstanding the irregularities shown in Fig. 4, the foaming volume measurements supported the desirability of maintaining a low moisture content in stored sugar–egg powders. During a previous study (1), it was noted that sugar–egg powder with a high moisture content had a higher foaming volume after short storage periods than low moisture powder. However,

after the powders had been stored for some time the foaming volume of the high moisture powder decreased below that of the low moisture powder. In the present study (Fig. 4) a similar effect was evident during storage at 40° F.

Effect of Methods of Packing

Of the powders stored at 40° F. for 52 weeks there was no evidence by any test to show that gas-packing had a preservative effect on the quality of

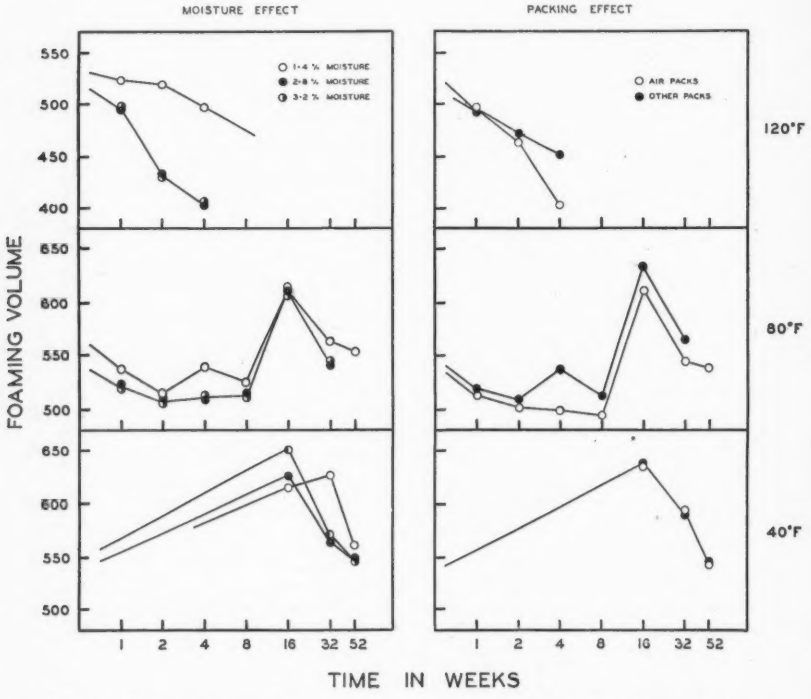

FIG. 4. *Effect of moisture contents of 1.4 to 3.2% and method of packing on the foaming volumes of dried sugar–egg powders.*

sugar–egg. At 80° F. the fluorescence test (Fig. 1) and the foaming volume test (Fig. 4) showed that the inert packs exerted some protective action during storage. However, pH (Fig. 3) and potassium chloride values (Fig. 2) were not affected by inert packing. Only pH and foaming volume measurements showed a beneficial effect from the use of inert packs on powders stored at 120° F. Although inert packs appeared to retard quality deterioration slightly, there was no evidence to show that any one was more effective than the other two. The limited protection provided by this treatment does not seem to warrant its use in current commercial practice.

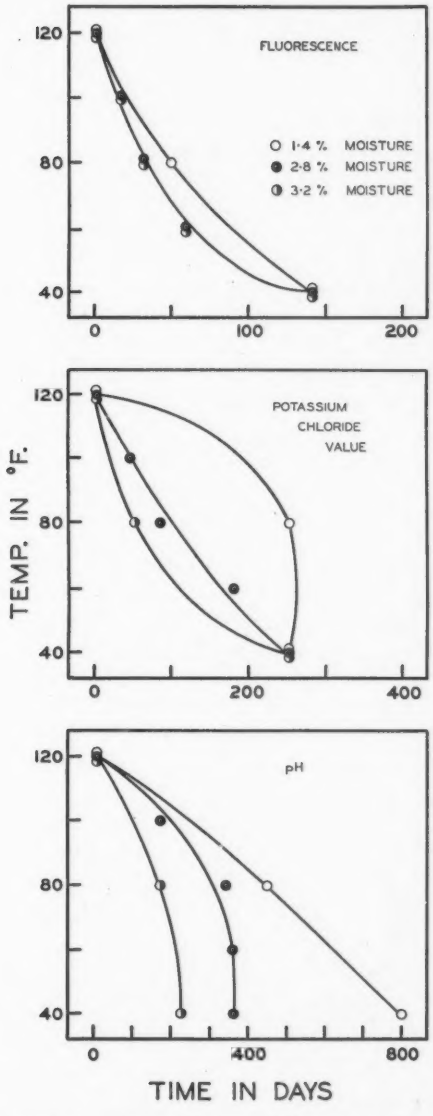

FIG. 5. *Effect of moisture contents of 1.4 to 3.2% on the time required for sugar–egg powder to change from A to B quality. Values plotted at 40°, 80°, and 120° F. were calculated from data in Figs. 1, 2, and 3; those at 60° F. were from the present study but not shown otherwise; those at 100° F. from a previous study (1).*

Discussion

The importance of moisture content in these powders can be assessed by considering the length of time required for them to change from *A* quality to *B* quality (shown by dotted lines in Figs. 1, 2 and 3 and summarized in Fig. 5) according to the tentative specifications for sugar–egg powder produced in Canada (6). Reducing the moisture content from 2.8 to 1.4% appeared to have little effect on the fluorescence and potassium chloride values of powder stored at 40° F.; perhaps, at this temperature, the protective effect of added sugar (1) was sufficient to mask any advantage gained from a very low moisture content. However, the pH changes indicated that the life of Grade *A* egg powder stored at 40° F. might be prolonged for more than one year when the moisture was reduced from 2.8 to 1.4%. Unless sugar–egg powder can be kept at temperatures of about 40° F. it seems advisable from these results to prepare powders with moisture contents below 2.8%, which are believed to be commercially feasible (2).

A previous investigation with plain egg powder showed that only carbon dioxide had a beneficial effect (11). The presence of added sugar in the egg powder used in this study apparently retards the reaction that contributes most to egg powder deterioration (probably a sugar–protein reaction (3)) and permits oxidation reactions to become more important. Hence any protective effect was common to all methods of obtaining an inert pack.

Acknowledgment

The authors wish to express their appreciation of the assistance rendered by Mrs. Margaret Reid, Biochemist.

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LIQUID AND FROZEN EGG

III. SOME FACTORS AFFECTING THE QUALITY OF STORED FROZEN EGG[1]

By Jesse A. Pearce[2] and Margaret Reid[2]

Abstract

Liquid from eggs of various qualities packaged in Reynold's Metal A-10 and liquid from Grade *A* eggs in wax paper with and without added ice was frozen at −40° F. and stored at 10°, 0°, and −10° F. for 12 months. Examination of baking properties and changes in pH, fluorescence, and reducing sugar content indicated the desirability of using liquid from Grade *A* eggs, although liquid from Grade *C* and cracked eggs may also be satisfactory; and of limiting the storage period for frozen egg, stored at these temperatures, to about six months. It was also desirable to allow the frozen egg to age for a month or two before use; and to use a highly moisture resistant barrier at all storage temperatures, although the wax paper and ice combination may be satisfactory at 0° and −10° F. Reducing sugar content decreased with an increase in the number of bacteria and, in addition, this measurement appeared to be a good indication of the quality of liquid and frozen egg.

Introduction

Since the production of eggs is seasonal, it is frequently necessary to carry large stocks for six months of the year or longer. The perishable nature of this commodity demands attention to the manner in which it is stored. While eggs in the shell can be held for short periods, some other method of preservation is desirable. Preserving eggs by removing them from the shell, mixing the yolk and white, and freezing has been an important commercial process for many years. During the war years, a large proportion of Canada's eggs were exported in the dried form; nevertheless, about five million pounds was frozen for use by bakery and other trades, exclusive of the quantities frozen for subsequent drying. However, only limited information is available to describe the keeping quality of the frozen product and the chemical changes occurring during its storage.

It seemed advisable before beginning the studies described in this paper to consider some of the changes likely to occur in eggs. An examination of frozen egg stored for six years at a temperature of 0° to −5° F. showed that if eggs of good quality were frozen, the odour of the product did not change but, if poor quality eggs were frozen, the initial putrid odour seemed to intensify (12). Although there appeared to be an increase in ammoniacal nitrogen as eggs became inedible (15, pp. 223-234), it seemed unlikely that this test would prove useful (15, pp. 260-261) and this was substantiated by preliminary work in these laboratories. As eggs deteriorate there is an increase in formic, lactic, and acetic acid content (5); therefore, measure-

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ments of pH changes seemed desirable. During work on dried eggs, it was observed that the fluorescence of extracts of the powder was related to the quality (9). Further work has indicated that fluorescence development may be attributed, in part, to a reaction between reducing sugars and proteins (1, 6, 7). Therefore, two modifications of this fluorescence test were applied to liquid eggs (10). It also appeared desirable to measure changes in reducing sugar content of the eggs, since this component has an important effect on the keeping quality of dried eggs (13) and since reducing sugars might disappear if the foregoing reaction occurred. In addition, sugar might also be removed by microbial growth (15, pp. 233-234). Much of the commercial frozen egg is used by the baking trade, and, for this reason, sponge cakes were believed desirable as tests of baking quality.

Materials and Methods

The storage experiment utilized material described in an earlier paper (10, Table IV). In brief, liquid from fresh Grade *A* eggs, from Grade *A* eggs held for 16 hr. at 80° F. in sterile glass containers, from Grade *C** eggs, from cracked eggs, from musty eggs, and from "eight-day" incubator reject eggs (for grade descriptions, see (2)) was poured into moulds containing about four litres, frozen within 16 hr. in a room operating at −40° F. and held at temperatures of 10° (+ 2°, − ½°), 0° (± 1°), and − 10° (± 1°) F. for a period of one year. Samples were examined before and after freezing, and after 3, 6, and 12 months' storage. The liquid from fresh Grade *A* eggs was packed in Reynold's Metal A-10, a highly moisture vapour resistant material (16), plus a Fourdrinier kraft, B-Flute carton; in waxpaper (40 lb. kraft, waxed to 50 lb.) plus the carton with ice cubes (about 2 cu. in. in volume) inside the carton around the wrapped egg; and in wax-paper and carton without added ice. All other samples were packed in Reynold's Metal A-10 and cartons.

The analyses included measurements of pH and reducing sugar (4, pp. 416 and 438) on whole egg liquid; fluorescence of whole egg liquid, using a modification of a technique applied to egg powder (3); and baking volume and foaming volume measurements on whole egg liquid (11). In one portion of the study, reducing sugar content and pH of liquid egg, before and after freezing, were compared with the viable bacterial count (14).

In the initial stages of the study, pH, reducing sugar and fluorescence measurements were made on sera removed from the frozen egg by the chloroform treatment described earlier (10). It was possible to collect enough sera for all measurements on samples up to and including the three-month storage period. At the six-month storage period, only enough serum was separated from any one sample to permit fluorescence evaluation. The fluorescence changes up to the six-month sampling have been discussed (10) and at the 12-month storage period, the structure of the frozen egg had so changed that no sera could be separated.

** Eggs may be graded as C because of dirty shells or because of poor quality before the candling lamp (2); those used in this study were selected for poor quality.*

Results

Effect of Bacterial Growth Before Storage on Reducing Sugar Content and pH

The relations between bacterial growth, reducing sugar content, and pH changes in frozen and unfrozen liquid egg are shown in Table I. Bacterial growth was most rapid in egg yolk and least rapid in egg white but both whole egg and egg yolk attained about the same bacterial populations after holding for 48 hr. at 80° F. Slight bacterial growth in liquid from whole egg and egg

TABLE I

THE RELATIONS BETWEEN REDUCING SUGAR CONTENT, pH, AND BACTERIAL GROWTH IN FROZEN AND UNFROZEN EGG

Material and treatment	Viable bacteria at 37° C.		Reducing sugar, %		pH	
	B.F.*	A.F.*	B.F.	A.F.	B.F.	A.F.
Whole egg						
48 hr. at 30° F.	$<1.0 \times 10^2$	1.0×10^2	0.32	0.28	7.7	8.1
24 hr. at 80° F. and 24 hr. at 30° F.	4.2×10^4	2.2×10^4	0.29	0.26	7.7	8.0
48 hr. at 80° F.	1.1×10^9	1.8×10^8	0.05	0.05	5.9	6.0
Egg white						
48 hr. at 30° F.	5.3×10^3	2.0×10^3	0.32	0.33	8.9	8.9
24 hr. at 80° F. and 24 hr. at 30° F.	4.6×10^3	7.7×10^3	0.32	0.32	8.5	8.3
48 hr. at 80° F.	7.0×10^4	2.2×10^5	0.29	0.25	8.2	8.3
Egg yolk						
48 hr. at 30° F.	5.0×10^2	5.0×10^2	0.24	0.26	6.4	6.4
24 hr. at 80° F. and 24 hr. at 30° F.	1.4×10^6	1.4×10^6	0.24	0.27	6.4	5.9
48 hr. at 80° F.	5.9×10^8	3.0×10^8	0.04	0.06	5.0	4.9

**B.F.—Before freezing. A.F.—After freezing.*

white had a more marked effect on the sugar content than on pH, while, for separated yolk, fairly excessive bacterial growth had little effect on either measure. Freezing appeared to effect slight reduction in the bacterial content of some samples, and to have little effect on pH or reducing sugar content of liquid from egg white, but caused an apparent reduction in the reducing sugar content of liquid from whole egg and an apparent increase in the reducing sugar content of liquid from yolks.

Quality Changes During Storage

Baking volume, foaming volume, pH, and fluorescence measurements on the whole egg liquid were of little value in differentiating between many of the stored samples and were of less value in differentiating between storage temperature and between method of packaging. Baking or foaming volume measurements were of value in demonstrating the effect of storage time.

Volume measurements on sponge cakes made from the various types of liquid egg showed that musty eggs and incubator rejects were less suitable

than the other types of egg (Fig. 1). Liquid egg before freezing or frozen egg stored for three months gave larger cakes than egg just after freezing. At the six-month sampling, the baking volume was slightly less than that at the three-month sampling and at the twelve-month sampling it was markedly

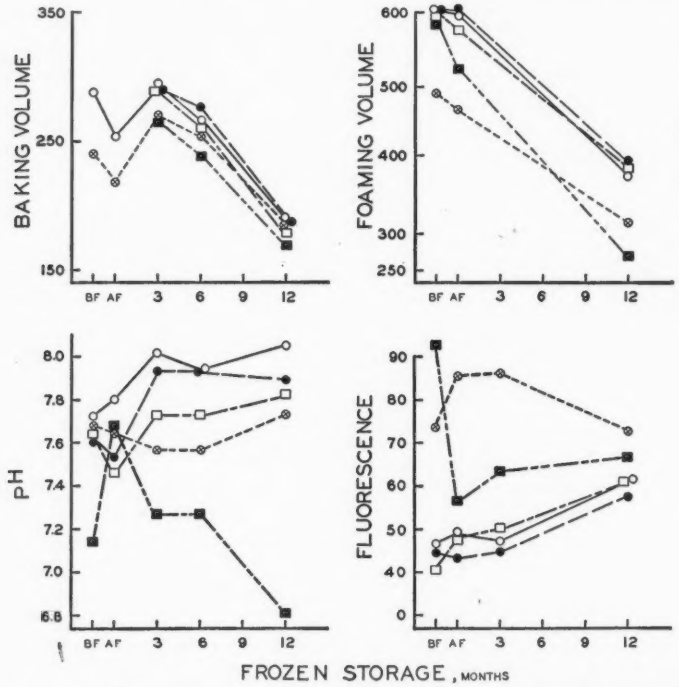

FIG. 1. *Effect of freezing and frozen storage on baking volume (ml.), foaming volume (ml.), pH, and fluorescence of liquid from eggs of varying quality.* ○ *Grade A.* ● *Grade C.* □ *Cracks.* ■ *Musties.* ⊕ *Incubator rejects.*

less. This reduction in the baking volume of egg when freshly frozen is known to occur in commercial practice and, in this state, the product is known as "green egg." Many concerns handling frozen egg prefer to let it age for a short period before releasing it.

Foaming volume measurements also showed that musty eggs and incubator rejects were less likely to be satisfactory in baked goods (Fig. 1). After 12 months' storage, egg held at 10° F. averaged 25 ml. less than the samples held at 0 or −10° F. Egg wrapped in Reynold's Metal A-10 and stored at 10 and 0° F. had foaming volumes 30 ml. greater than when wrapped in waxed paper (with or without added ice): at −10° F. no difference was evident.

Musty eggs were generally more acidic than incubator rejects, which in turn were more acidic than all other types of egg studied (Fig. 1). All types

of frozen egg, except that prepared from musty eggs, tended to become more alkaline as the storage time increased. Liquid from musty eggs increased in pH markedly during the freezing period and then decreased rapidly as storage progressed. Liquid from Grade *A* eggs suffered smaller pH increases when stored at −10° F. than when stored at 0° and 10° F. (Table II).

TABLE II

SOME EFFECTS OF TEMPERATURE ON THE QUALITY OF FROZEN EGG

Criteria	Type of eggs	Temperature, °F.	Storage time				
			B.F.*	A.F.*	3 Mos.	6 Mos.	12 Mos.
pH	Grade *A*	10	7.72	7.80	8.02	8.03	8.11
		0			8.08	7.87	8.08
		−10			7.92	7.90	7.95
Fluorescence	Incubator rejects	10	73.5	85.4	83.0	—	60.1
		0			88.0	—	76.1
		−10			86.0	—	80.9
	Musty	10	92.8	56.6	64.0	—	75.9
		0			62.0	—	62.0
		−10			64.0	—	61.4

**B.F.—Before freezing. A.F.—After freezing.*

The fluorescence of material from Grade *A*, Grade *C*, and cracked eggs was generally lower than that of musty eggs and incubator rejects and showed a general increase through freezing and frozen storage, with the fluorescence value of Grade *A* and cracked eggs somewhat higher than the values for Grade *C* eggs (Fig. 1). The high fluorescence values of liquid from Grade *A* and cracked eggs when compared to those of liquid from Grade *C* eggs may reflect differences between measurements directly on the melange and measurements on the serum (10), or may be only a reflection of the limited number of samples of eggs used. In an earlier study, more comprehensive on this point, liquid from Grade *C* eggs, on the average, resulted in powders with fluorescence values higher than those of liquid from Grades *A* and *B* eggs (8).

Incubator rejects gave a product that increased in fluorescence during freezing and decreased in this attribute during frozen storage, while musty eggs gave a product that decreased in fluorescence during freezing and increased during frozen storage (Table II). The decreases for reject egg and the increases for musty egg were more rapid at + 10° F. than at 0° and −10° F. While the fluorescence changes in the liquid from incubator rejects are at present unexplainable, the fluorescence and pH changes in musty egg may be related to commercial observations. If pails of liquid have a musty odour and are allowed to stand for about 24 hr. at 30° F., the musty odour will disappear. It is possible that the volatile products are acid in nature and

highly fluorescent. However, loss of these volatiles did not improve baking quality. An attempt is being made, in these laboratories, to isolate the possible acid, fluorescing volatiles.

Measurements of the reducing sugar content appeared to be of greater value than the foregoing and are shown in more detail (Fig. 2). These measure-

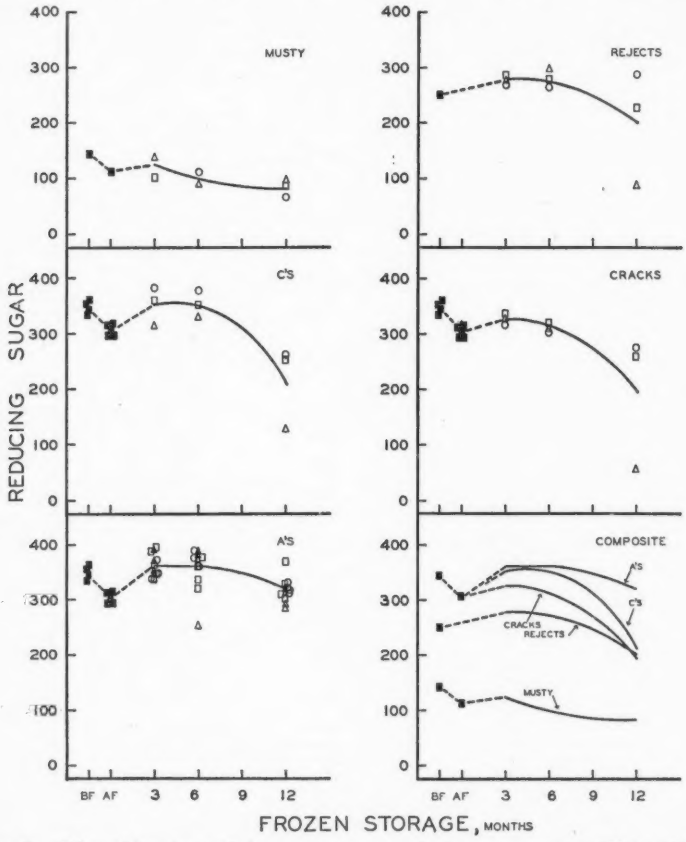

FIG. 2. *Effect of freezing and frozen storage on reducing sugar content (% × 1000) of liquid from eggs of varying quality.* ■ *Values before (B.F.) and after freezing (A.F.).* △ *Storage at 10° F.* □ *Storage at 0° F.* ○ *Storage at −10° F.*

ments showed greater loss in sugar content as the storage temperature increased; as shown by the points in the figure, however, only mean changes for the various types of egg are given by the curves. The apparent decrease in reducing sugar content after freezing, observed in the preliminary study, was again noted here. This was followed by an increase after three months' storage but after six months' storage reducing sugar again decreased. These changes corresponded in general with the changes in baking volume.

The reducing sugar content was greatest for liquid from Grade *A* eggs and decreased for liquid from the other types in the following order: Grade *C*, cracked, incubator reject, and musty eggs. The reducing sugar values reported here for fresh liquid egg are in general agreement with some values reported in the literature, but lower than others (15, pp. 230 and 249). Measurements of reducing sugar appear to be a good indication of egg quality and they can be readily performed in a plant laboratory or by local consulting laboratories.

TABLE III

EFFECT OF PACKAGING METHOD ON FREEZER BURN IN FROZEN EGG STORED 12 MONTHS

Packaging method*	Approximate depth of dehydrated surface, in., at various temperatures		
	10° F.	0° F.	−10° F.
All samples in Reynold's Metal A-10	0	0	0
Liquid from Grade *A* eggs in wax paper plus ice chunks	>1	0	0
Liquid from Grade *A* eggs in wax paper only	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$

** All further enclosed in kraft carton.*

The effect of freezer burn on the frozen blocks is described in Table III. The greatest general protection was afforded by the Reynold's Metal wrap. The addition of chunks of ice reduced freezer burn at storage temperatures of 0° and −10° F. but appeared to accelerate freezer burn at + 10° F. The latter effect may be attributable to differences in specific heat of the ice and the liquid egg, resulting in transfer of moisture from the blocks of frozen egg to the ice as the temperature of the storage room and its contents varied around the controlled temperature, 10° (+ 2°, $-\frac{1}{2}$°) F.

Acknowledgments

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DRIED MILK POWDER

VI. THE EFFECT OF GAS- AND VACUUM-PACKING ON KEEPING QUALITY[1]

By Jesse A. Pearce[2] and W. A. Bryce[3]

Abstract

Skim (1% fat) and whole (26, 28, and 30% fat) milk powders (2% moisture) from two plants were packed in air, carbon dioxide, nitrogen, 80% carbon dioxide and 20% nitrogen, 20% carbon dioxide and 80% nitrogen, and under vacuum, and stored for 12 months at 80° F. Quality was assessed by a tasting panel of 14 persons. Packing in an inert gas or under vacuum effected a general improvement in the quality of skim-milk powders. This was attributed to removal of volatile degradation products during the packing process and early storage. The storage life of whole milk powders was increased from a maximum of three months when packed in air to nine months when packed in inert gases or vacuum.

Introduction

Packing milk powders in nitrogen or carbon dioxide or in mixtures of both has become common commercial practice, but the effectiveness of these gases for preserving milk powders has been the subject of some controversy. The use of nitrogen only was reported to have no beneficial effect (14), but other investigations indicated that it provided protection (15), particularly if the oxygen concentration of the headspace gas was maintained at a low level (5, 8). The use of carbon dioxide has been variously reported as favourable (8, 15), without beneficial effect (14, 16), and harmful (7) to stored, dried, whole milk. Other reports indicated that mixtures of these two gases provided protection to stored milk powders (3, 6) and that packing under vacuum or partial vacuum had a beneficial effect on stored milk powders (7, 14, 15).

Studies on dehydrated egg-and-milk mixtures have shown that packing in carbon dioxide extends the storage life of this product (13). Carbon dioxide had a greater preservative effect on stored egg powder than nitrogen, which was in turn better than air (12).

The above results show that marked disagreements exist in the published investigations on the effect of gas-packing on the storage life of dried milk. It was, therefore, deemed advisable to compare the effect of packing in air, carbon dioxide, nitrogen, mixtures of carbon dioxide and nitrogen, and under vacuum, on milk powders of different fat levels from different sources. The present paper describes this investigation.

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Materials and Methods

The materials used were those described in an earlier paper of this series (1) and consisted of powders of 1, 26, and 28% butterfat from one plant and powders of 1, 26, 28, and 30% butterfat from another. The powders were tempered to a moisture content of 2% by vacuum desiccation over phosphorus pentoxide and were packed in tinplate containers.

Occluded air (oxygen) may effect the storage life of gas-packed milk powder (3, 6, 8, 9). Therefore, in the packing technique used, an attempt was made to reduce the occluded gas to a minimum and to have the same amount in each sample. Using a previously described apparatus (2), the chamber containing the tins was evacuated to 1 mm. pressure, flooded with gas of the desired composition, evacuated as before, flooded again, and sealed. In vacuum packing, the tins were held under 1 mm. pressure for 15 min. and sealed at this pressure. The gases used were nitrogen, carbon dioxide, 80% carbon dioxide and 20% nitrogen, and 20% carbon dioxide and 80% nitrogen. Although it is believed that carbon dioxide may not be an "inert" gas when used to protect stored fat (7), the gas and vacuum-packs will be grouped under the heading "inert packs."

The foregoing samples and control samples with air as the headspace gas were stored at 80° F. and examined by palatability assessment initially and after 1, 3, 6, 9, and 12 months. To assess palatability, the samples were reconstituted as previously described (10), and sampled by 14 tasters. Scoring was done on a scale of 10 (the equivalent of excellent, fresh whole or skim-milk) to 0 (repulsive). A score of 4 is considered the point at which milk is no longer suitable for use as a milk drink. The reliability of the scoring by the taste panel has been estimated and palatability assessment was found to be more suitable than any of the chemical tests of milk powder quality (10). The desirability of using organoleptic tests as well as chemical tests on stored milk powders has been observed by others (4).

Results

The scores for the skim-milk powders (1% butterfat) at the 1 to 12 month samplings and scores for the whole milk powders (26, 28, and 30% butterfat) at the 1 to 9 month samplings were subjected to analysis of variance. The factors found to be significant are shown, in Fig. 1, by curves drawn through the mean palatability values for the various sampling times.

As noted previously, these skim-milk powders improved in quality during the first month of storage (1). Contrary to these earlier results (1), skim-milk powders from the two sources, when stored in an atmosphere of air, did not differ significantly in quality, but after 12 months' storage in inert atmospheres or in vacuum the powder from Plant 2 was considered half a palatability unit better than powder from Plant 1. Although no one method of obtaining an inert pack was significantly better than any other, after 12 months' storage, skim-milk powders in inert packs were significantly better than the air-packed material (about one palatability unit).

The air-packed whole milk powders deteriorated in a manner similar to that previously described (1); powders of 26 and 28% fat from Plant 2 had the poorest keeping quality; powder of 30% fat was better; and powders of 26 and 28% fat from Plant 1 had the best storage life. As observed in the previous study (1), there was no significant difference between powders of 26 and 28% fat from either plant.

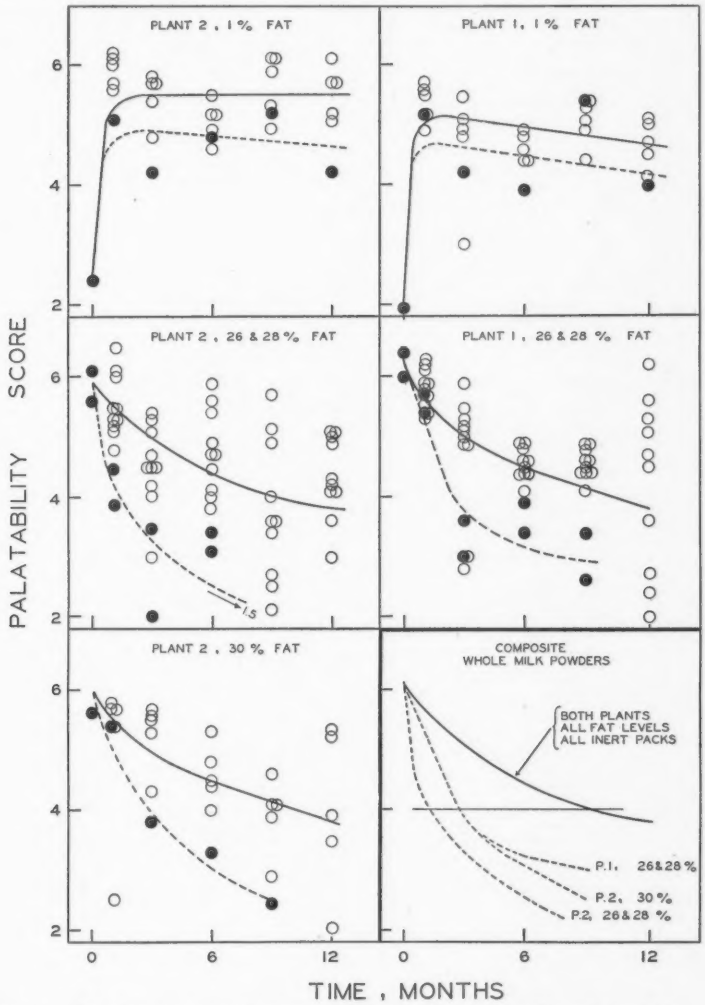

FIG. 1. *The effect of gas- and vacuum-packing on skim and whole milk powders stored at 80° F.*

——○—— *gas- or vacuum-packed material.*

- - - - - - - - - - ● - - - - - - - - - - *air-packed material.*

The average loss in quality was the same in all whole milk powders packed in an inert atmosphere or under vacuum. No one method of obtaining an inert pack lengthened storage life significantly more than any other. However, the use of inert packs extended the average life of whole milk powders, normally one to three months, to nine months.

Discussion

The consistently higher palatability scores for the skim-milk powders packed in inert atmospheres and under vacuum support a previous suggestion that degradation products, responsible for low quality, are dissipated during the first few weeks after repacking (11). Beneficial effects of inert packing were evident after one month, and this superiority was maintained throughout the storage period. It is possible that subjecting these powders to low pressures during repacking removed quantities of volatile degradation products in excess of those dissipated when repacking in air only.

The variation in the rate of quality deterioration of the air-packed whole milk powders shows the effect on fat stability of processing practice in the different plants. Gas- or vacuum-packing reduced this difference in fat stability. While dissipation of degradation products may have been partly responsible for this improved storage life of gas- or vacuum-packed whole milk powders, the increasing differences in palatability, as storage progressed, supports previous evidence (5, 8) that reduction in the oxygen content of the gas surrounding the powder particles minimizes deterioration.

Deteriorative changes in whole milk powders packed in inert atmospheres approached those of air-packed skim-milk powder. This and other factors (11) indicated that solids-not-fat also play an important role in the deterioration of whole milk powders.

A wide variation was observed in the scores applied to the powders packed in inert gases or under vacuum. This variation includes the effect of a number of factors: source of powder, fat level, method of obtaining an inert pack, variability in the milk powder samples, and variability of taster scores. These results may explain the observed differences in effectiveness of methods of gas-packing. Examination of the scatter shows that some samples in inert packs were judged to be of lower quality than air-packed samples, while others were considered to be about the same quality as the air-packed samples. Therefore, it is possible that samples in inert packs, when examined by one investigator, might appear no better than air-packed samples, while another examination would show inert packing to have a beneficial effect. The results presented here show that the average effect of inert packing is a prolongation of the storage life of dried milk powder.

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A STUDY OF METHODS FOR ASSESSING RANCIDITY IN LARD[1]

By G. A. Grant[2] and H. J. Lips[3]*

Abstract

Lard from 26 sources was stored in glass jars at 26.7° C (80° F) until definitely rancid. Spoilage was evaluated at two-week intervals by chemical tests and odour ratings. Correlation coefficients between odour scores and the logarithms of chemical test values were: iodometric peroxide, −.90; alpha-dicarbonyl test, −.85; Stamm test −.82; Kreis test −.81; ferrometric peroxide, −.80; fluorescence, .79; free fatty acids, −.10. Association between chemical measurements was greatest between alpha-dicarbonyl and iodometric peroxide values (r = .97). As peroxides are not thermostable, the measurement of the stable alpha-dicarbonyl compounds, although less precise, is considered the best available chemical method for assessing rancidity.

Introduction

Recent increases in production and export of Canadian lard have focused attention on the perishability of the product. As part of a program to improve the stability and general quality of lard, a study was made of available chemical methods for detecting rancidity. A number of these methods and their association with odour ratings are described in the present paper.

Methods

The exact measurement of rancidity development in fats by any one procedure is difficult. This is due to the diversity of the reactions producing rancidity, e.g., atmospheric oxidation and the action of micro-organisms and enzymes. Taste and smell, among the least sensitive of the senses, have been widely used as criteria of rancidity but since odour and taste judgments are difficult to reproduce, it is desirable to employ chemical or physical measurements, which are reproducible and can be calibrated against the results of odour or taste panels.

Considerable uncertainty exists concerning the relative merits of the chemical tests and only those showing promising results from preliminary trials were selected for the present study. These included determination of peroxide oxygen, Kreis, Stamm, alpha-dicarbonyl, and fluorescence values.

Peroxide Oxygen Content

Several methods have been proposed for determining peroxides in fats (1, 5, 6, 11, 22). A modification (6) of an iodometric method (10) and a modification (11) of a ferrometric method (1) were selected. The iodometric is

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simpler than the ferrometric procedure but the latter has been reported to be more sensitive.

A previous study on chicken fat indicated that peroxide oxygen content as determined by the iodometric procedure was 20% less than the actual content (2) because iodine was absorbed by the unsaturated fatty acids. As lard has an appreciably lower iodine number than chicken fat, it was assumed that this correction was not necessary. Lea's original practice (10) of reporting peroxide oxygen as millilitres of 0.002 *N* sodium thiosulphate is employed in this investigation for the iodometric procedure. The peroxide content by the ferrometric method (11) is reported as milliequivalents of peroxide per kilogram of fat.

Kreis Value

Of the several modifications of the Kreis test (9) one (20) was selected because of its simplicity and because the colour was developed in a single phase system. The colour intensity has been found proportional to the concentration of fat (21), increasing with a decrease in fat concentration. For this investigation the same concentration of fat, 1 gm. in 10 ml., was adopted for all determinations, dilution, if necessary, being made in the coloured solution. The Evelyn photoelectric colorimeter (3) was used for all colorimetric procedures. The colour intensity of the Kreis test was determined using a No. 540 mμ Rubicon filter, and reported as extinction coefficients according to the equation $E = \frac{2-\log G}{C}$, where G is the corrected galvanometer reading and C is the concentration of fat in grams per millilitre of final solution. Although this value has little physical significance it is suitable for purposes of comparison.

Alpha-dicarbonyl and Stamm Values

Many tests for rancidity depend on the presence of aldehydes and ketones in the oxidized fat. Of the many methods for the detection of aldehydes and ketones in rancid fat (4, 8, 12, 16, 17), two (12, 17) were chosen for further study.

The Stamm method (17) used arbitrary standards to measure the colour developed, and was not sensitive to small changes in colour intensity. Use of a colorimeter was believed desirable to obtain accurate comparison between samples. The reagent was prepared by heating 0.5 gm. of *s*-diphenylcarbazide in 100 ml. of tetrachloroethane until it dissolved, cooling rapidly, and filtering in a darkened room. It was then stored in a brown reagent bottle. Heating 1.0 gm. of fat with 10 ml. of reagent in a graduate for 3.0 min. at 100° C., cooling rapidly, and reading immediately in the Evelyn colorimeter employing a 580 mμ filter was found to be satisfactory. The results are reported as extinction coefficients.

The alpha-dicarbonyl method (12) was also modified for use with the Evelyn colorimeter. Preliminary test solutions containing 1.0 gm. of fat, 1.0 ml. of 30% potassium hydroxide solution, and 9.0 ml. of ethanol heated for 20 min. at 60° C., demonstrated differences between fresh and rancid lard.

However, the solutions were not suitable for reading in the colorimeter, as they separated into two phases. Employing stronger potassium hydroxide solution or heating for one hour failed to produce a single phase system, but with the use of 30 ml. of alcohol the solutions remained clear and in a single phase.

To investigate the effect of fat concentration on the extinction coefficient, 0.5, 1.0, and 3.0 gm. of lard were heated with 3.0 ml. of potassium hydroxide solution and 32 ml. of purified ethanol. The solution containing 3.0 gm. of lard became cloudy and had to be filtered. The ethanol was freed of aldehydes and ketones by refluxing with calcium oxide, distilling, shaking with 2,4-dinitrophenylhydrazine and redistilling. The results are given in Table I. The extinction coefficient decreased with an increase in fat concentration and 1.0 gm. of fat showed the largest difference between fresh and rancid lard.

TABLE I

THE EFFECT OF FAT CONCENTRATION ON EXTINCTION COEFFICIENTS IN THE ALPHA-DICARBONYL TEST

Weight of sample, gm.	Extinction coefficients	
	Fresh	Rancid*
0.5	3.2	7.1
1.0	0.9	5.4
3.0	0.9	3.7

** The peroxide oxygen content of the rancid sample was 14 ml. of 0.002 N thiosulphate per gm.*

The effects of temperature and time of heating were also investigated. Solutions were heated for 30 min. at 60° C. and 100° C. and for 30, 60, and 90 min. at 80° C. The results are shown in Tables II and III. Raising the

TABLE II

THE EFFECT OF TEMPERATURE AFTER HEATING FOR 30 MIN. ON THE ALPHA-DICARBONYL EXTINCTION COEFFICIENTS

Temperature, °C.	Extinction coefficients	
	Fresh	Rancid
60	0.2	9.4
80	0.7	8.4
100	0.4	9.1

temperature from 60° to 100° C. had little effect on the extinction coefficient, but increasing the time of heating resulted in a higher value. This effect was more pronounced in fresh lard than in the rancid samples.

The procedure adopted was as follows. One gram of fat was weighed into a glass-stoppered graduate and 3 ml. of 50% potassium hydroxide solution and 30 ml. of purified ethanol were added. The solution was heated for 30

TABLE III

EFFECT OF TIME OF HEATING AT 80°C. ON ALPHA-DICARBONYL EXTINCTION COEFFICIENTS

Time, min.	Extinction coefficients	
	Fresh	Rancid
30	0.72	8.4
60	1.70	8.9
90	2.12	9.2

min. at 80° C., then allowed to cool, made up to 35 ml. with alcohol, and read in an Evelyn colorimeter using a 420 mμ filter. The results were reported as extinction coefficients.

Fluorescence

Examinations of lard by ultra-violet light have been reported (13; 19, pp. 90-91). A method (13) using the Coleman photofluorometer standardized with quinine sulphate as previously described (14) was investigated. Fluorescence values are reported as photofluorometric readings of the lard solution minus blank solvent readings.

From previous work on butterfat (7) it was indicated that the type of solvent and concentration of fat might have a marked influence on the fluorescence values. To study the effect of organic solvents on fluorescence of fresh and rancid lard, 1.0 gm. of lard was dissolved in 10 ml. of various solvents, slightly warmed, mixed thoroughly, and read on the photofluorometer. Petroleum ether, xylene, dioxane, benzene, and ethylene dichloride were studied, as the previous work had indicated a better differentiation between rancid and fresh fat with these solvents. The results are given in Table IV. The rancid lard gave lower fluorescence values with all solvents.

TABLE IV

THE EFFECT OF ORGANIC SOLVENTS ON THE FLUORESCENCE OF FRESH AND RANCID LARD

Solvent	Fresh	Rancid
Petroleum ether	14.0	12.0
Xylene	19.5	12.0
Dioxane	16.5	8.7
Benzene	16.0	8.0
Ethylene dichloride	15.5	11.5

Greater differences were observed with dioxane, benzene, and xylene than with petroleum ether or ethylene dichloride. Xylene was chosen for further study as it gave the lowest blank reading.

To study the effects of concentration, 1- to 5-gm. samples of fresh or rancid lard were dissolved in 10 ml. of xylene. The results are given in Table V.

TABLE V

THE EFFECT OF CONCENTRATION ON THE FLUORESCENCE OF FRESH AND RANCID LARD

Weight, in gm. per 10 ml. of solvent	Fluorescence value	
	Fresh	Rancid
1	13.7	8.7
2	27.5	12.2
3	37.2	15.0
5	Over 100	16.0

An increase in fat concentration gave an increase in fluorescence values. This increase was of greater magnitude with fresh lard than with the rancid samples. As the fluorescence changes between the fresh and rancid lard were not similar with dilution, an empirical method was adopted to ensure comparability. One gram of fat was weighed into a 10 ml. glass-stoppered graduate and 10 ml. of xylene added. The mixture was shaken until the fat was completely dissolved and then read in a Coleman photofluorometer.

Odour Tests

Rancidity in the lard was assessed by a 10 member panel and scored on the following basis: 10, excellent, odour fresh or absent; 8, good, no rancid odour; 6, fair, slight rancid odour; 4, poor, odour definitely rancid; 2, bad, odour very rancid; 0, unapproachable. Odours that could be classified as burnt, tanky, or otherwise objectionable, but not rancid, were given a rating of 7 on this scale.

Materials and Procedure

Samples of all types of lard manufactured in Canada were received from 26 Canadian packing plants and stored in half-pint glass jars at 26.7° C. Ten samples were put into storage every two weeks and sampled at two-week intervals. This ensured differences in level of rancidity, and convenience in the number of samples coming out of storage at any one time. Samples for odour tests were removed and the remainder melted on a steam-bath and mixed thoroughly to provide material for the objective tests. If all the tests were not completed on the day of sampling the material was stored at −40° C.

Results

The association between objective tests and the odour test was assessed by computing simple correlation coefficients. For predicting odour scores from objective test values, the correlation coefficient must be highly significant and attain a value of .8 to .9. A small scatter around the regression line is also desirable and this was assessed by computing the error of estimate. The coefficients of correlation with their errors of estimate and prediction equations between odour score and the logarithms of the objective tests are given in Table VI.

TABLE VI

THE CORRELATION COEFFICIENTS, PREDICTION EQUATIONS, AND ERRORS OF ESTIMATE BETWEEN ODOUR SCORE AND LOGARITHMS OF THE OBJECTIVE TEST DATA

Quantities correlated with odour score:	Degrees of freedom	Correlation coefficients	Prediction equations	Errors of estimate
Alpha-dicarbonyl	204	−.85	$y = 8.48 - 2.78x$	0.83
Iodometric peroxide oxygen	160	−.90	$y = 7.63 - 1.81x$	0.70
Ferrometric peroxide oxygen	204	−.80	$y = 8.30 - 1.52x$	0.94
Kreis	183	−.81	$y = 10.0 - 2.73x$	0.54
Stamm	204	−.82	$y = 7.67 - 2.01x$	0.91
Free fatty acids	108	−.10	—	—
Fluorescence	191	.79	$y = 5.53 + 6.63x$	0.96

A decrease in odour score was associated with an increase in all the objective values, except the fluorescence measurements, which gave a corresponding decrease. Of the objective tests correlated with rancidity as assessed by odour scores, the alpha-dicarbonyl values and peroxide oxygen determined by the iodometric procedure gave the highest associations. The Kreis, Stamm, ferrometric peroxide oxygen, and fluorescence values were all about equally associated with odour score. The sensitivity of the tests as assessed by the regression coefficients showed the ferrometric peroxide oxygen to be most sensitive. However, this test and the fluorescence measurement had the two largest errors of estimate. The fluorescence values, although highly associated with odour score, had regression values too high to enable prediction of odour scores lower than 5.0 (Fig. 6), the fluorescence values being almost nil at this point. This indicates that fluorescing substances were almost completely destroyed when the lard had just become rancid. The free fatty acid values were not significantly associated with odour scores.

Further details of the association between objective tests and odour scores are shown in Figs. 1 to 6. The equations for the relations shown in the figures are given in Table VI. It is evident from Figs. 1 to 6 and Table VI that a slightly rancid lard (odour score of 6) corresponded to the following objective test values: alpha-dicarbonyl value, 7.8; iodometric peroxide oxygen, 7.8; ferrometric peroxide oxygen, 31.6; Kreis value, 28.8; and Stamm value 6.8. The regression lines of the objective tests are shown in Fig. 6. The two

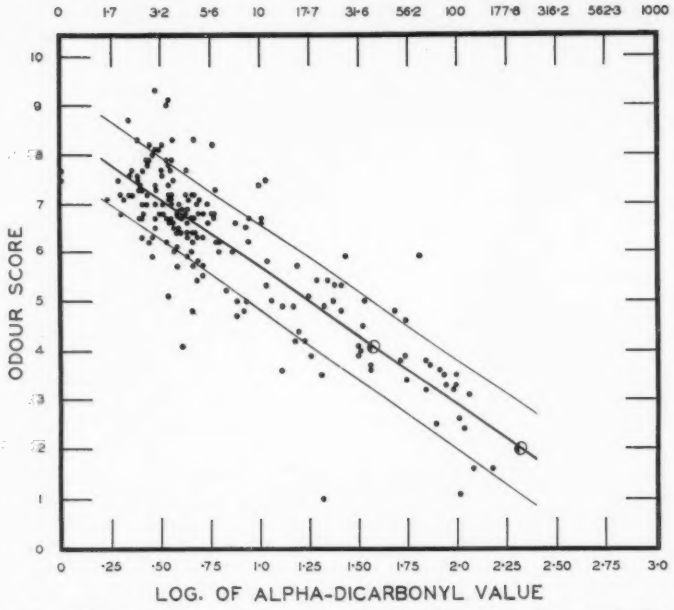

FIG. 1. *Relation between odour score and alpha-dicarbonyl value on development of rancidity in lard stored at 80° F.*

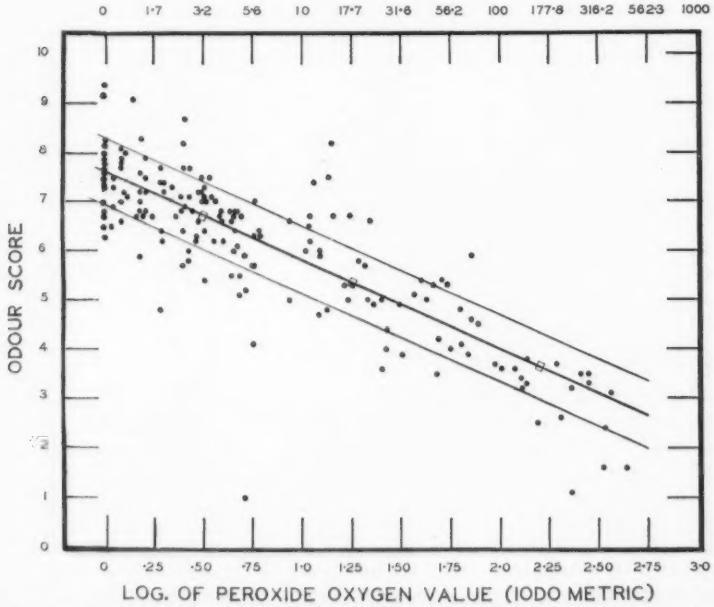

FIG. 2. *Relation between odour score and iodometric peroxide oxygen content on development of rancidity in lard stored at 80° F.*

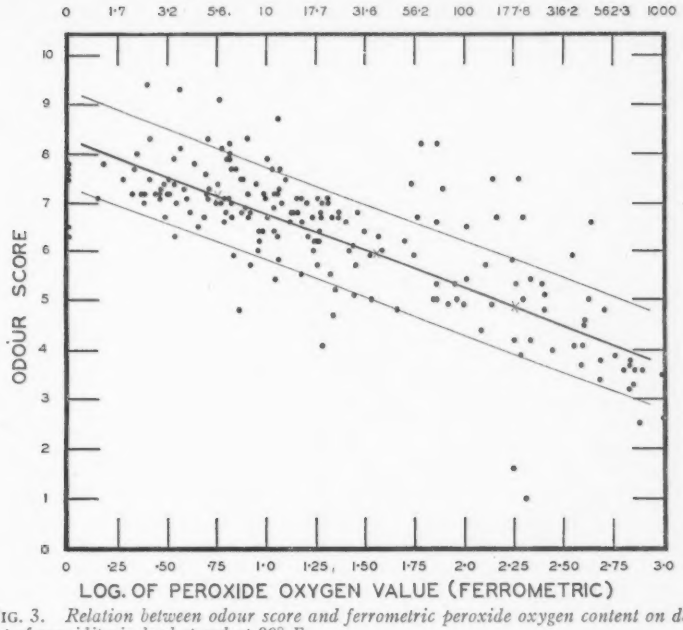

FIG. 3. *Relation between odour score and ferrometric peroxide oxygen content on development of rancidity in lard stored at 80° F.*

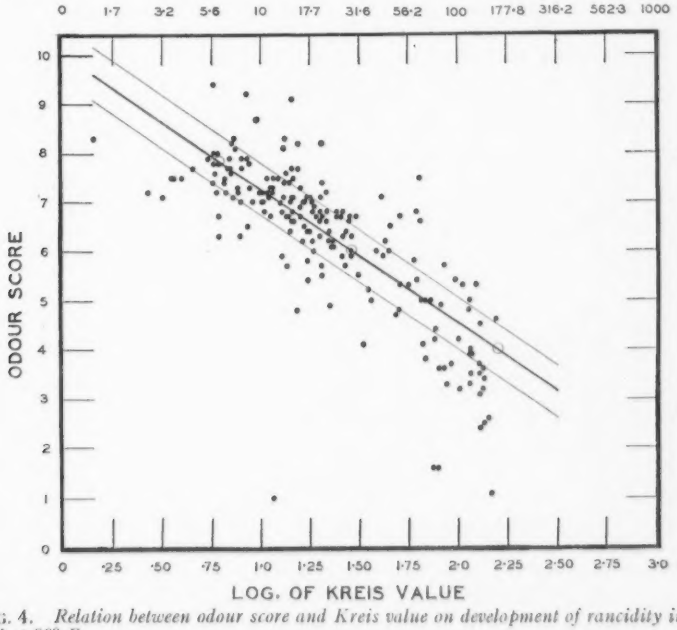

FIG. 4. *Relation between odour score and Kreis value on development of rancidity in lard stored at 80° F.*

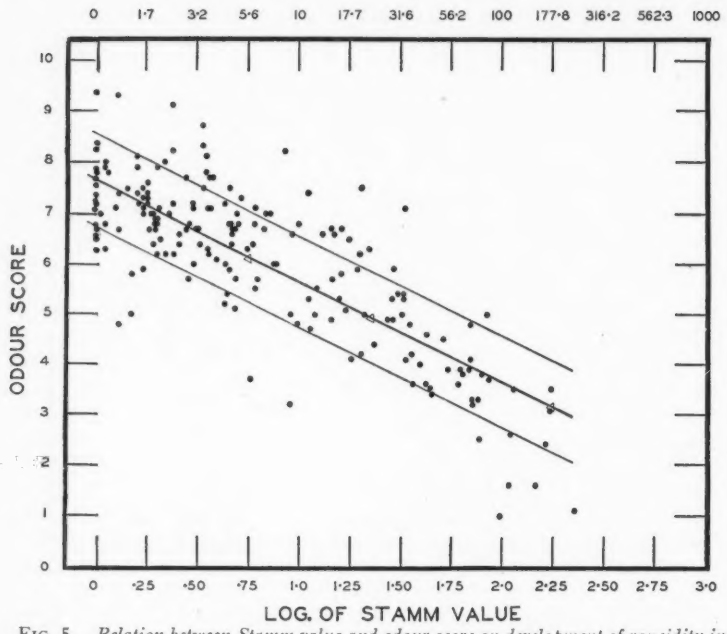

FIG. 5. *Relation between Stamm value and odour score on development of rancidity in lard stored at 80° F.*

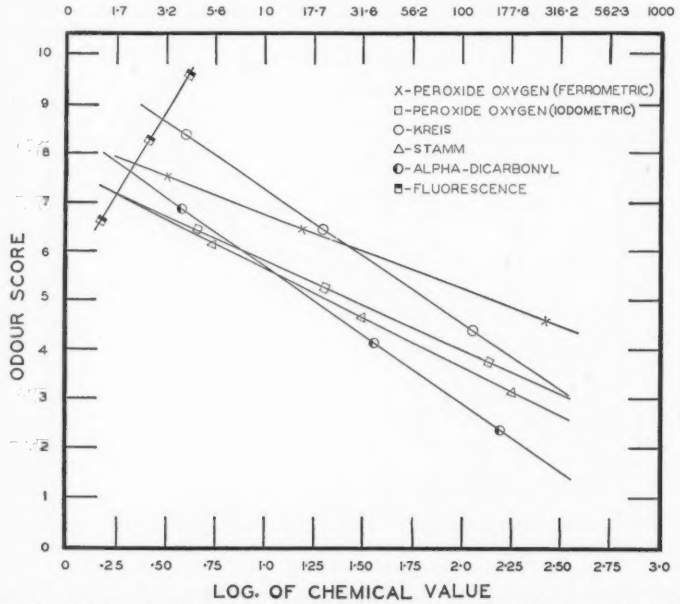

FIG. 6. *Relation of regression lines of the objective tests and odour score in lard which developed rancidity on storage at 80° F.*

peroxide methods gave the same slope. The Kreis and alpha-dicarbonyl measurements also showed equal slopes, but of greater magnitude than those of the peroxide values.

Interrelation of Chemical Measurements

The interrelation of the chemical measurements was assessed by computing simple correlation coefficients (Table VII). Of the methods investigated, the

TABLE VII

SIMPLE COEFFICIENTS OF CORRELATION BETWEEN OBJECTIVE TESTS ON LARD THAT ATTAINED STATISTICAL SIGNIFICANCE

Quantities correlated	Degrees of freedom	Correlation coefficients
Alpha-dicarbonyl value with:		
Iodometric peroxide oxygen content	204	0.97**
Ferrometric peroxide oxygen content	204	0.86**
Stamm value	204	0.60**
Logartithm of alpha-dicarbonyl value with:		
Kreis value	198	0.89**
Iodometric peroxide oxygen content with:		
Stamm value	204	0.62**
Ferrometric peroxide oxygen content	204	0.84**
Logarithm of iodometric peroxide oxygen with:		
Logarithm Kreis value	198	0.90**
Ferrometric peroxide oxygen content with:		
Stamm value	204	0.60**
Logarithm of ferrometric peroxide oxygen with:		
Kreis value	204	0.57**
Stamm value with:		
Kreis value	204	0.73**

** *Indicates 1% level of statistical significance.*

alpha-dicarbonyl value and peroxide oxygen content were most closely associated. The Kreis values showed a logarithmic association with alpha-dicarbonyl and peroxide oxygen content. The results suggest that formation of peroxides is more closely associated with alpha-dicarbonyl compounds, believed present in increasing quantities in rancid fat (16), than with epihydrin aldehyde, which may also be present (15), and which is supposedly responsible for the Kreis test.

Discussion

Although most of the results of the chemical methods were highly associated with those of organoleptic rancidity, the peroxide oxygen and alpha-dicarbonyl measurements appeared to have more advantages than the others. As peroxides are not thermostable, the peroxide oxygen content is usually altered by

processing techniques such as deodorizing or bleaching. Thus, substantial oxidation may have taken place, but the material may have only a small peroxide value. The measurement of the stable alpha-dicarbonyl compounds although less precise is considered a better method for the assessment of rancidity.

It is of interest to note the disappearance of fluorescent materials with the appearance of rancid odours at the end of the induction period. This indicates that fluorescence in lard may be linked with natural antioxidant substances, which are altered by oxidation.

Acknowledgments

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A FLUORESCENCE METHOD FOR ASSESSING THE KEEPING QUALITY OF BUTTER[1]

By G. A. Grant[2] and W. Harold White[3]

Abstract

The fluorescence values of serum from salted butter were affected by separation temperature, dilution, nature and pH of the diluent, and the stability of the diluted serum. A satisfactory procedure was as follows. The serum was separated by placing 125 gm. of butter in centrifuge bottles and heating to 45° C. in a boiling water-bath, centrifuging at 1700 r.p.m., and siphoning off the fat. Two millilitres of the serum was diluted to 50 ml. with 10% sodium acetate, the pH adjusted to 5–6 and the fluorescence determined immediately in a Coleman photofluorometer using a filter that transmitted light in the region of 365 mμ. This procedure gave fluorescence values that were correlated with flavour score ($r = -.84$) on salted butter stored at 32.2° C. (90° F.).

Introduction

Numerous objective methods for assessing the quality of butter have been investigated without marked success. These include measurements of the aldehyde (9), peroxide (7), and free fatty acid (2) contents of the fat; and titratable acidity, hydrogen ion concentration, and amino nitrogen content of the serum (2). The measurement of fluorescence has been applied to a variety of foodstuffs (3, 4, 5) to assess the changes induced by storage. Concomitant organoleptic assessment of the products has shown marked relation between flavour deterioration and fluorescence values for some materials, e.g., powdered eggs, while for others the objective test is not at all indicative of flavour status. This is to be expected since, for the materials studied, fluorescence is an attribute of the salt extract of the defatted material and as such primarily reflects changes in the non-fat components. Increasing the moisture content of egg powder and ration biscuits (8, 3) brought about an increase in fluorescent material, and in the latter suppressed oxidative changes in the fat. These observations suggested that the serum separated from butter would contain fluorescing substances in amounts that increase as the butter deteriorates. This paper describes the factors affecting the measurement of fluorescence in fresh and spoiled salted butter, and demonstrates the changes in fluorescence value under accelerated storage conditions.

Procedure

Preliminary Trials

After several trials it was observed that serum and butter fat could be separated satisfactorily by heating 125 gm. of butter at 60° C. for five minutes

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and centrifuging for 10 min. at 1700 r.p.m. The fat was removed by siphoning and the clearest portion of serum pipetted into an Erlenmyer flask.

One millilitre of serum was diluted to 20 ml. with one of the solutions to be described, thoroughly mixed, and passed through No. 1 Whatman filter paper. The fluorescence of a 15 ml. portion of the filtrate was determined by means of a Coleman photofluorometer with standard 'Vitamin B_1' filters transmitting active light of wave-length 365 mμ. The photofluorometer was standardized by adjusting the instrument to give a scale reading of 50 for a solution containing 0.20 γ of quinine sulphate per ml. (5).

Effect of Diluents

During preliminary trials it was observed that when sera from fresh and spoiled samples of salted butter were diluted with 10% potassium chloride solution their fluorescence values differed by 38 photofluorometer units. These sera were turbid, presumably owing to dispersion of fat particles. It was believed that fat solvents mixed with other diluents for the serum might eliminate this difficulty. However, mixtures of dioxane, acetone, and chloroform with various salt solutions proved unsatisfactory. A number of diluents when used by themselves showed promise and merited further investigation.

An aqueous solution of sodium acetate was found to be the most satisfactory solvent because it gave the greatest difference in fluorescence readings between fresh and spoiled butter (viz., 45.0 and 65.6, respectively) and the solution was only slightly turbid. The sodium chloride, ammonium chloride, and ethyl alcohol solutions gave satisfactory differences but were too turbid. Sodium acetate, sodium chloride, ethyl alcohol solutions, and water were selected for further study.

Effect of pH

Hydrogen ion concentration has been shown to have an effect on the fluorescence of an extract of defatted dried egg powder (6). In the present study, pH effects were evaluated using the selected diluents mentioned above. Water and solutions of sodium chloride and ethyl alcohol were adjusted to the desired pH by adding dilute hydrochloric acid or sodium hydroxide solution; the pH of the sodium acetate solution was adjusted with dilute acetic acid or sodium hydroxide.

The diluted sera from spoiled butter increased in turbidity with increase in pH between 4 and 9, while that from fresh butter remained fairly clear. At pH 2 all the diluted sera were quite clear but fluorescence values were small. Sera, diluted with sodium acetate solution adjusted to pH 5, resulted in the clearest extracts, and a large difference in fluorescence values between fresh and spoiled butter (viz., 16.0 and 87.0, respectively). Therefore, a 10% solution of sodium acetate adjusted to pH 5–6 was selected as an appropriate diluent and used in all subsequent work.

Effect of Temperature

It was observed in the above study that duplication of results was poor in some instances. Since it had been demonstrated that temperature affected

the fluorescence of extracts of dried whole egg powder (6), it was considered that temperature variations might be responsible for the difference between duplicates. To evaluate this the procedure was modified as follows: samples of butter placed in centrifuge bottles and heated in a boiling water-bath were centrifuged when the samples were at each of the following temperatures: 35°, 40°, 50°, 60°, and 80° C. Fluorescence values were determined for each sample as previously described.

The results showed that temperature had little effect on the fluorescence of sera from fresh butter, but an increase in temperature caused a small decrease in fluorescence of sera from spoiled butter. The greatest difference in fluorescence values between fresh and spoiled butter (viz., 26.0 and 35.0, respectively) was obtained for sera separated by heating to 40° or 50° C. Hence heating to 45° C. in a boiling water-bath prior to centrifuging was believed desirable.

Effect of Dilution

The fluorescence of a solution may be quenched by various factors, such as too great a concentration of fluorescing substance, which may be avoided by proper dilution. Such procedures may introduce other errors, namely, quenching or apparent quenching due to the solvent or instrument error (10). Therefore, it was of value to determine behaviour of butter sera diluted to various concentrations.

One-millilitre aliquots of serum, obtained from a sample of spoiled butter, were diluted to the following volumes with 10% sodium acetate solution (pH 5–6): 20, 30, 40, 50, 60, 70, 90, 100, and 200 ml. Fluorometric readings on these solutions are shown in Fig. 1. At the higher concentration there is slight quenching, as the relation deviates from the linear. Therefore solutions should be diluted so that readings will fall between 10 and 70 fluorescence units.

Stability of Diluted Sera

The time elapsing between dilution of a serum and photofluorometric measurement might conceivably affect the fluorometric value obtained. To study this, serum obtained from spoiled butter was diluted 1 : 50 with 10% sodium acetate of pH 5–6, allowed to stand at room temperature, and fluorometric values determined at intervals throughout a six-hour period. The data show that the diluted serum is reasonably stable at room temperature, since there is a decrease of only five fluorometer units (viz., 45.0 to 40.0) in six hours.

Recommended Procedure

As a result of the above observations the following procedure was adopted as being most suitable. Whole salted butter (125 gm.) weighed into a centrifuge bottle was heated to 45° C. with constant stirring in a boiling water-bath,

and centrifuged for 10 min. at 1700 r.p.m. Fat and serum were separated by centrifuging and siphoning off the fat. Two millilitres of clear serum was diluted to 50 ml. with 10% sodium acetate solution (pH 5–6), mixed, and filtered through No. 1 Whatman filter paper. The fluorometric value of the

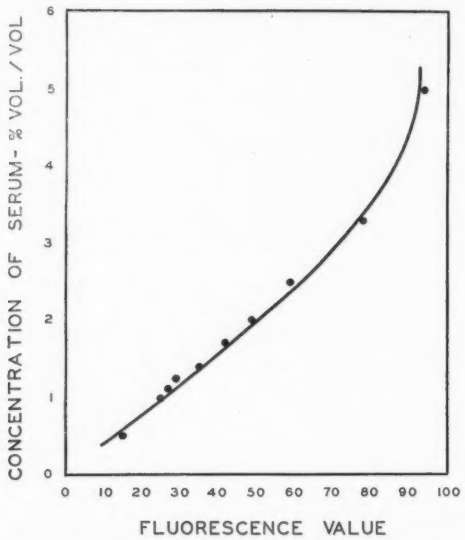

FIG. 1. *Effect of dilution on the fluorescence value of spoiled butter serum.*

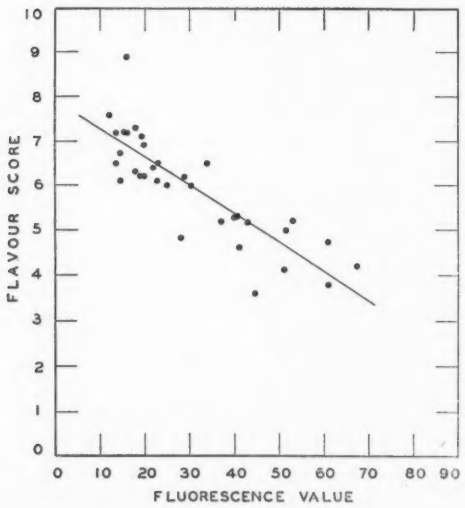

FIG. 2. *Relation between flavour score and fluorescence values on samples of stored butter.*

filtrate was determined in a Coleman photofluorometer. As the diluent had a small fluorescence value it was necessary to correct all fluorescence readings.

Evaluation of the Method on Stored Butter

Materials and Methods

The material investigated consisted of four sets of samples of canned and printed salted butter from an eastern and a western Canadian creamery. The butter was stored at 32.2° C. (90° F.) for 32 days and sampled at intervals to give a wide range of quality. To assess the suitability of the fluorometric method, fluorescence values were compared with flavour scores. The usual method for scoring butter was not employed as it is not readily adaptable to statistical treatment. Butter was scored as follows: 10, excellent; 8, good; 6, fair; 4, poor; 2, bad; 0, inedible. The ten tasters were required to score a set of four samples chilled to approximately 10° C. (50° F.).

Results

Fluorescence values increased with a decrease in flavour score (Fig. 2). Good agreement is indicated between the two ($r = -.84$). The equation for these data is:

$$y = 7.867 - 0.0632\,x,$$

where x = corrected photofluorometer readings and y = flavour score. It is evident that fluorescence values of 30 and 61 correspond to flavour scores of 6 and 4, respectively.

Statistical analyses of the data obtained for each sample of butter showed a high correlation and no difference between regression coefficients. There was no significant increase in correlation by using the log of fluorescence values, which is the usual form of curve to be expected. However, this may possibly be due to insufficient samples of low and high flavour scores. The co-linearity of the four sets of data was slightly different. While this difference was statistically significant it is probable that the taster level of scoring did not remain constant.

Discussion

The high correlation and lack of significant difference in regression coefficients between fluorescence measurements and flavour scores indicate that this test should be a valuable aid in assessing the keeping quality of butter under unfavourable storage temperatures. However, this test will not assess flavour deterioration in butter due to tainting by foreign materials, nor can it be definitely stated whether it will apply to other forms of spoilage that may occur in commercial practice (1, pp. 75-92).

Acknowledgments

The authors wish to thank Mr. D. B. W. Reid for statistical computations and Miss Wanda B. Price and Miss J. R. Lewis for technical assistance.

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THE BACTERIAL FLORA OF LOW-ACID VEGETABLES CANNED AT 212° F.

II. A PRELIMINARY STUDY OF THE EFFECTS OF EXTRACTS FROM PROCESSED TOMATO JUICE AND FROM TOMATO PLANTS ON BACTERIA INVOLVED IN FOOD PRESERVATION[1]

J. W. CONNER[2]

Abstract

Commercially processed tomato juice, dehydrated tomato stems, leaves, seed, and fruit (variety, Sutton's Very Earliest), and tomato seedlings (variety Pan America), were extracted with methanol and the extracts tested for antibacterial properties against certain species of bacteria important in the food industries, and other Gram-positive and Gram-negative types. The extracts prepared from tomato juice and tomato fruit inhibited the growth of most of the test organisms.

Introduction

The fact that certain plant extracts possess antibacterial properties has been known for some time. Burkholder (1) reported that extracts of 27 species of lichens possessed antibacterial properties. C. S. Pederson and P. Fisher (6) found that the expressed juices of certain cabbages inhibited the growth of *Leuconostoc mesenteroides*, *Lactobacillus plantarum*, and *Lactobacillus brevis*. In 1944, Lucas and Lewis (5) reported antibacterial principles in the expressed juices of *Onopordon acanthium* (Scotch thistle), *Verbascum thapsus* (common mullein) and *Paeonia officinalis* against *Staphylococcus aureus*. The same authors also found antibacterial principles in some varieties of *Lonicera tatarica* (one of the honeysuckles) active against both *Staphylococcus aureus* and *Escherichia coli*.

The discovery by Irving, Fontaine, and Doolittle (3) of 'lycopersicin', a fungistatic agent from the tomato plant, suggested that the tomato juice used in processing low-acid vegetables (1) might contain an antibiotic agent capable of suppressing the growth of certain micro-organisms. Irving, Fontaine, and Doolittle (3) reported that 'lycopersicin' inhibited the growth of *Fusarium oxysporum* (Fusarium Wilt) when tested by the cylinder-plate method.

In the light of these discoveries, extracts of canned tomato juice and of tomato plants at various stages of growth were prepared and tested against certain species of bacteria important in the food industry, and other Gram-positive and Gram-negative types.

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Contribution from the Department of Bacteriology, Ontario Agricultural College, Guelph, Ont. Submitted in partial fulfilment of the requirements for the degree of Master of Science in Agriculture in the Graduate School of the University of Toronto, June 1946.

[2] *Lecturer.*

Methods

It was originally intended to isolate from tomato juice a material similar to that obtained by Irving, Fontaine, and Doolittle (3) from Pan America and other varieties of tomato plants. Their technique (3), with certain necessary modifications, was followed in the isolation of the active principle. Untreated, filtered, and dehydrated samples of commercially processed tomato juice were examined. Methanol extracts of the leaves, stems, seeds, and fruit (green, partially ripe, and ripe) of mature tomato plants (variety, Sutton's Very Earliest), and of tomato seedlings (variety, Pan America) were prepared, and the extracts evaporated to dryness. The residue was taken up, in some instances with sterile distilled water, and, in others, with sterile phosphate buffer solution. In a number of experiments with tomato juice filtrates, the pH was raised to 5.40 and 7.08 prior to extraction. The chemicals used in the extractions were tested and did not show antibacterial activity.

The aerobic test organisms used were *Bacillus thermoacidurans* (A.T.C.C. No. 8038), *Bacillus subtilis* (Penicillin resistant), *Bacillus subtilis* (penicillin sensitive), *Escherichia coli*, *Eberthella typhosa*, *Lactobacillus lycopersici* (A.T.C.C. No. 4005), *Salmonella aertrycke*, *Salmonella anatis*, *Salmonella enteritidis*, *Salmonella morgani*, *Salmonella paratyphi*, *Salmonella psittacosis*, *Salmonella schottmuelleri*, *Salmonella typhimurium*, *Serratia marcescens*, *Shigella dysenteriae*, *Shigella flexneri*, *Shigella gallinarum*, *Shigella sonnei*, *Staphylococcus aureus*, and *Staphylococcus citreus*. The anaerobic bacteria tested were *Clostridium butyricum*, *Clostridium thermosaccharolyticum* (A.T.C.C. No. 7956), and *Clostridium sporogenes* (A.T.C.C. No. 3679). All the trial organisms were not used with the various extracts, owing to the small amount of extract available. With the aerobes, the cylinder-plate method was employed in testing the extracts and a modification of the thioglycollate agar dilution technique of Lock (4) was used for the anaerobes.

Results

Untreated and Filtered Tomato Juice

Preliminary experiments with untreated tomato juice and tomato juice filtrate employing the cylinder-plate technique were conducted. Both the plain tomato juice and the filtered juice inhibited the growth of *S. citreus*, producing zones of inhibition measuring 13 mm. in diameter. Very little, if any, inhibition of the growth of *B. subtilis* was evidenced. However, the organisms did not grow directly under the liquid in the cylinders.

Dehydrated Tomato Juice and Pulp

Commercially processed whole tomato juice and pulp filtered from tomato juice, dehydrated at 55° C., yielded extracts possessing antibacterial properties against several species of bacteria. The results are presented in Table I. The extracts were tested by the cylinder-plate technique. This crude extract inhibited the growth of the test organisms when used undiluted and when diluted 1 to 1 or 1 to 2 with sterile distilled water or with sterile phosphate

TABLE I

AVERAGE DIAMETERS OF ZONES OF INHIBITION PRODUCED BY EXTRACTS FROM DEHYDRATED TOMATO JUICE AND PULP

Test organisms	Zones of inhibition, mm.		
	Not diluted	Diluted 1 : 1	Diluted 1 : 2
B. subtilis (penicillin resistant)	29.5	25.0	16.0
B. subtilis (penicillin sensitive)	21.0	19.0	11.0
E. coli	21.3	17.5	16.0
E. typhosa	32.0	28.0	18.5
L. lycopersici	21.5	14.0	Nil
S. aertrycke	37.0	29.0	19.0
S. analis	21.0	17.0	11.0
S. enteritidis	24.0	17.0	12.5
S. morgani	25.0	21.0	14.0
S. paratyphi	18.5	18.0	12.5
S. psittacosis	37.5	28.5	21.5
S. schottmuelleri	20.0	16.5	9.5
S. typhimurium	21.0	19.5	Nil
S. marcescens	18.5	10.5	9.0
S. dysenteriae	32.0	28.0	24.0
S. gallinarum	25.0	21.5	18.5
S. flexneri	40.5	32.0	21.0
S. sonnei	30.0	23.5	16.5
S. aureus	30.5	25.5	14.0
S. citreus	42.6	32.5	29.0

buffer. The zones of inhibition decreased with dilution of the extract. It is interesting to note that the phosphate buffer alone inhibited the strain of *S. citreus* used, producing a zone of inhibition measuring 22 mm. in diameter. The other organisms were not affected by the buffer solution.

Tomato Juice Filtrate

Several extractions were prepared using commercially processed tomato juice, which was filtered through filter paper. The diameters of the zones of inhibition produced against the test organisms by these crude filtrates are presented in Table II. In general, when the pH of the filtered juice was raised to 5.40 and 7.08, and when the phosphate buffer was employed as the medium for dissolving the principle, the zones of inhibition produced were more extensive than those produced by the principle dissolved from the final residue in sterile distilled water. These results are presented in Table III. Since most of the extractions were qualitative, it is difficult to compare accurately separate extractions. However, it would appear from Tables I and II that the extracts prepared from dehydrated juice were more active than those from the filtrate.

The growth of the same test organisms was inhibited by filtrate and dehydrated juice extracts. In most cases, a zone of increased growth surrounding the clear zone of inhibition appeared on the plates. In greater dilutions the extract apparently acted as a stimulant to bacterial growth. This phenomenon is particularly noticeable with *S. marcescens*. A typical

TABLE II

AVERAGE DIAMETERS OF ZONES OF INHIBITION PRODUCED BY EXTRACTS FROM TOMATO JUICE FILTRATE

Test organisms	Zones of inhibition, mm.		
	Not diluted	Diluted 1 : 1	Diluted 1 : 2
B. subtilis (penicillin resistant)	20.5	16.5	14.5
B. subtilis (penicillin sensitive)	34.0	22.0	19.0
B. thermoacidurans	12.0	9.0	Nil
E. coli	19.0	14.5	10.0
E. typhosa	25.0	23.0	22.0
L. lycopersici	29.5	15.0	14.0
S. aertrycke	19.5	14.0	10.0
S anatis	21.0	19.0	17.5
S enteritidis	29.5	22.0	20.5
S. morgani	20.5	18.0	14.5
S. paratyphi	26.0	23.0	20.0
S. psittacosis	27.0	25.0	19.0
S. schottmuelleri	25.0	18.0	20.5
S. typhimurium	27.0	23.0	17.5
S. marcescens	14.0	10.5	9.0
S. dysenteriae	25.5	19.5	17.5
S. gallinarum	21.5	18.0	15.0
S. flexneri	20.0	19.0	16.0
S. sonnei	17.0	14.0	12.5
S. aureus	15.5	15.0	9.0
S. citreus	27.5	24.0	23.0

TABLE III

AVERAGE DIAMETERS OF ZONES OF INHIBITION PRODUCED BY VARIOUS EXTRACTS FROM TOMATO JUICE FILTRATE

Organisms	pH prior to extraction	Diluent	Zones of inhibition, mm.	
			Undiluted	Diluted 1 : 1
B. subtilis		Phosphate buffer	31.0	25.0
	5.40	Sterile distilled water	16.5	14.0
	7.08	Sterile distilled water	14.0	10.0
E. coli		Phosphate buffer	34.6	23.6
	5.40	Sterile distilled water	13.0	10.0
	7.08	Sterile distilled water	11.0	10.0
S. marcescens		Phosphate buffer	18.3	10.5
		Sterile distilled water	13.0	—
	5.40	Sterile distilled water	12.0	11.0
	7.08	Sterile distilled water	13.0	10.0
S. aureus		Phosphate buffer	33.3	25.3
	5.40	Sterile distilled water	13.0	11.0
	7.08	Sterile distilled water	10.0	9.0
S. citreus		Phosphate buffer	37.3	27.6
		Sterile distilled water	24.0	—
	5.40	Sterile distilled water	28.0	26.0
	7.08	Sterile distilled water	24.0	19.0

example shows a clear zone of absolute inhibition measuring 13 mm. in diameter. Surrounding this zone, and covering a surface area of 1 mm. diameter, was a zone of moderate growth, followed by a 9 mm. zone of extremely heavy, raised, moist, and shiny growth. Beyond this, a 7 mm. zone of less than average plate growth appeared, merging gradually to the average amounts of growth on the agar, distant from the cylinder. With *S. citreus*, a plate showing a clear zone of 29 mm. possessed a 5 mm. zone in which the growth was very heavy and then average growth over the remainder of the plate.

Tomato Plants

The seeds, roots, stems, and leaves of tomato plants (variety, Sutton's Very Earliest), grown under glass, did not, under the conditions of these experiments, possess an appreciable amount of the active principle obtained from the tomato juice and fruit. The only exception was one extract prepared from a mixture of dehydrated leaves and stems, which produced a very small zone of inhibition with *S. marcescens*.

The results obtained with extracts from tomato seedlings (variety, Pan America) were inconclusive. One extract failed to inhibit the growth of *B. subtilis*, *Bacillus stearothermophilus*, *B. thermoacidurans*, *E. coli*, *S. aureus*, *S. citreus*, and *S. marcescens*. Another extract, also from Pan America seedlings, produced zones in which the inhibition of growth was doubtful with *B. subtilis*, *E. coli*, *S. citreus*, and *S. marcescens*.

Tomato Fruit

Thinly sliced tomato fruit (variety, Sutton's Very Earliest) was dried at 55° C. Methanol extracts of the dry residue contained the active principle. The first extract prepared from the partly mature tomatoes was tested on only three organisms, because of the small amount of buffered extract available. The extract was almost twice as active against the spore-forming, Gram-positive rod, *B. subtilis*, as it was against *S. aureus* and *S. marcescens*. This inhibition of *B. subtilis* is in contrast to the very slight inhibition obtained in the preliminary experiment using untreated tomato juice. Further tests with extracts prepared from ripe, partly ripe, and green fruits on several species of bacteria gave results comparable with those obtained with the tomato juice extracts. The extracts prepared from ripe fruits seemed more active than those obtained from partly ripe and green fruits (Table IV). In high dilutions, the extract from ripe tomatoes prevented the growth of *C. butyricum*, *C. sporogenes*, and *C. thermosaccharolyticum*. In most tests, when 3 ml. of the extract was diluted with 4 ml. of thioglycollate agar, these organisms failed to grow. In lower dilutions the extract stimulated growth, and with *C. butyricum* and *C. sporogenes* a larger amount of gas was produced than with the plain thioglycollate agar. (Plates I, II, and III show the inhibition of the growth of some bacteria by extracts from tomato fruit).

TABLE IV

AVERAGE DIAMETERS OF ZONES OF INHIBITION PRODUCED BY EXTRACTS FROM TOMATOES

Test organisms	Zones of inhibition in mm.		
	Undiluted	Diluted 1 : 1	Diluted 1 : 2
A* *B. subtilis* (penicillin resistant)	19.0	18.0	16.0
B. thermoacidurans	9.0	—	—
B. stearothermophilus	20.0	16.0	9.0
E. coli	25.0	22.0	13.0
S. aureus	22.0	23.0	21.0
S. citreus	36.5	30.0	22.0
S. marcescens	9.0	Nil	Nil
B† *B. subtilis* (penicillin resistant)	24.0	19.0	15.5
B. thermoacidurans	12.0	—	—
B. stearothermophilus	20.0	19.0	10.0
E. coli	27.0	11.0	—
S. aureus	20.0	14.0	10.0
S. citreus	26.0	17.5	20.5
S. marcescens	15.5	13.5	12.0
C‡ *B. subtilis* (penicillin resistant)	29.0	24.5	18.0
B. thermoacidurans	10.0	Nil	Nil
B. stearothermophilus	19.0	12.0	10.0
E. coli	17.5	14.0	10.0
S. aureus	21.0	21.0	18.5
S. citreus	19.0	14.0	11.0
S. marcescens	16.5	12.5	Nil§

* *Extract from green tomatoes.*

† *Extract from partly ripe tomatoes.*

‡ *Extract from ripe tomatoes.*

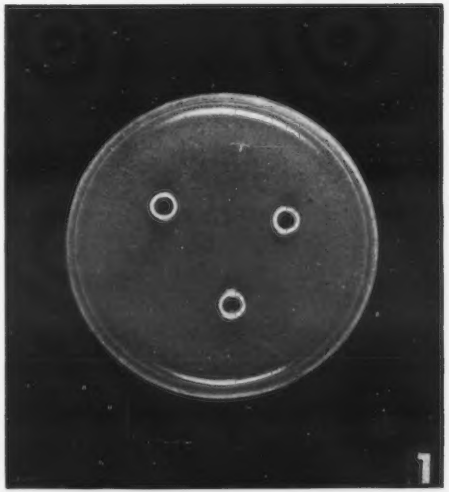
§ *5 mm. zone of heavy growth around cylinder with no pigment.*

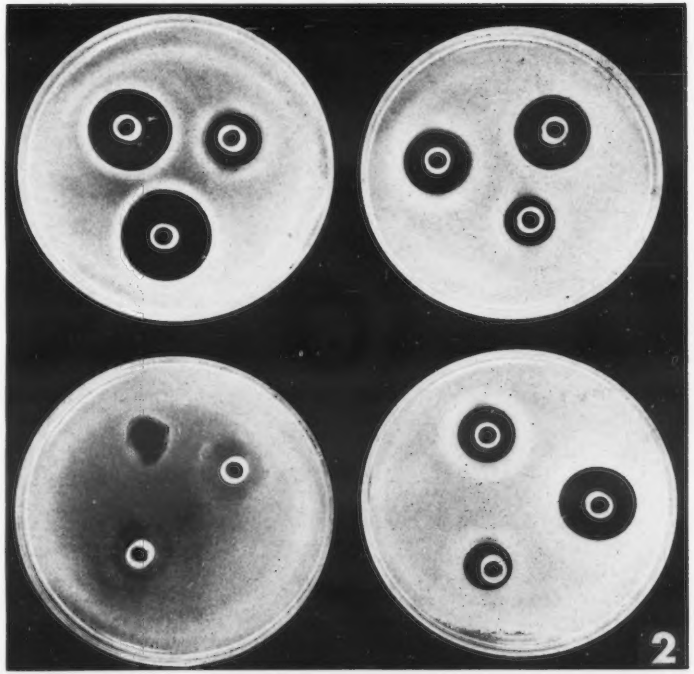
Discussion

It seems evident from these preliminary experiments that tomatoes contain a principle capable of antibiotic action. The principle obtained by the methanol extraction is active *in vitro* against both the Gram-positive and Gram-negative bacteria tested.

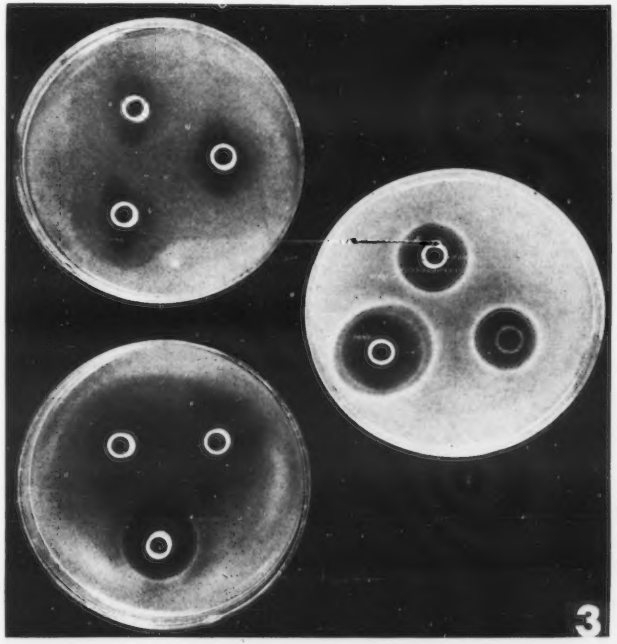
The principle is present mainly in the fruit and is not injured by the commercial processing of tomato juice. The presence of the principle in the seed, leaves, stems, or roots of tomato plants (variety, Sutton's Very Earliest) grown under greenhouse conditions could not be demonstrated. This would indicate that the principle obtained in this laboratory differed from 'lycopersicin.' Irving, Fontaine, and Doolittle (3), reported lycopersicin, a fungistatic agent from tomato plants, as being present in the stems, roots, and leaves, but not in the fruit or seeds.

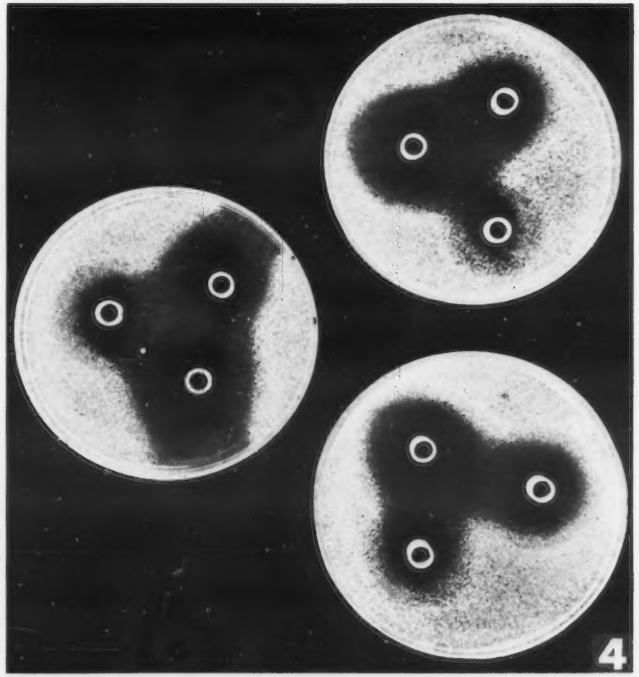
It seems probable that the lower surviving bacterial population obtained by the addition of 50% tomato juice to the covering solution in the processing of low-acid vegetables at 212° F. (2), might be due, at least in part, to an active bacteriostatic principle originating in the tomato fruit.





FIGS. 1 and 2. *Cylinder-plate assays of extracts from tomatoes.* FIG. 1. *Control plate inoculated with B. subtilis (penicillin resistant), and cylinders filled with sterile phosphate buffer.* FIG. 2. *Plates inoculated with B. subtilis and cylinders filled with extract (undiluted, diluted 1 : 1, and diluted 1 : 2) from tomato fruit (variety, Sutton's Very Earliest) and seedlings (Pan America). Upper left, extract from ripe fruit; upper right, extract from partly ripe fruit; lower right, extract from green fruit; and lower left, extract from tomato seedlings.*





FIGS. 3 and 4. *Cylinder-plate assays of extracts from tomatoes.* FIG. 3. *Plates inoculated with E. coli and cylinders filled with extract (undiluted, diluted 1 : 1, and diluted 1 : 2) from tomato fruit. Upper left, extract from green fruit; lower left, extract from partly ripe fruit; and right, extract from ripe fruit.* FIG. 4. *Plates inoculated with S. citreus and cylinders filled with extract from tomato fruit. Upper right, extract from partly ripe tomatoes; lower right, extract from green tomatoes, and left, extract from ripe tomatoes. (Note overgrowth on prolonged incubation with the extract diluted 1 : 2.)*

PLATE III

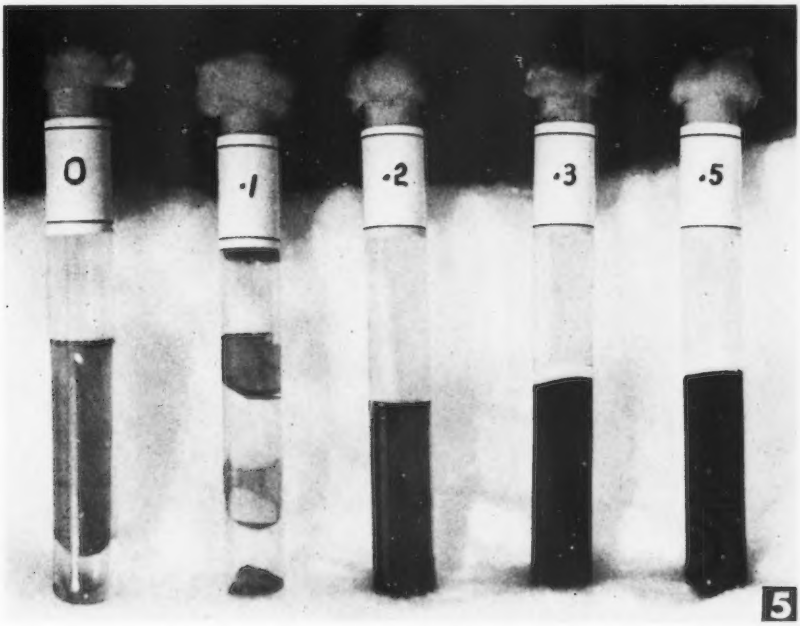


FIG. 5. *Effect of extract from ripe tomatoes on C. sporogenes inoculated into thioglycollate agar containing various amounts of the extract; 0.2 ml. of the extract mixed with 4 ml. of agar inhibited the growth of this test organism.*

Acknowledgments

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THE DYEING OF NATURAL COTTON WITH DIRECT DYES: SOME EFFECTS DUE TO TEMPERATURE, DYE CONCENTRATION, AND ANIONIC SURFACE-ACTIVE AGENTS[1]

R. P. GRAHAM[2] AND W. J. SEAGERS[3]

Abstract

The presence of an anionic surface-active agent in the dyeing of natural cotton yarn with a purified direct dye, using a dye-bath containing sodium chloride, is shown to increase the rate of dyeing, and to increase the amount of dye sorbed at equilibrium. The rate-accelerating effect has been studied as a function of the concentration of surface-active agent, using both commercial materials and methanol-extractable fractions of the latter. The effect exerted by an anionic surface-active agent, both on the equilibrium sorption and on the rate of dyeing, decreases as the temperature is increased. An explanation of the data, in terms of an interaction between the fibre and surface-active agent, is advanced.

Studies carried out in the absence of a surface-active agent show that with increased temperature of dyeing the rate of dye sorption is increased, but the value of the equilibrium sorption is decreased; the dyeing process in exothermic. The relation between equilibrium sorption and residual dye-bath concentration is expressible by a Freundlich equation, and that between equilibrium sorption and initial dye-bath concentration is linear, at least over the range of concentration studied. The time required to reach a state of equilibrium increases as the initial concentration of dye in the bath is increased.

Introduction

The discovery in 1884 that Congo Red was a substantive dye for cotton led to the development of a very large number of synthetic direct cotton dyes. The application of these dyes to cellulosic materials has been extensively studied since the late nineteenth century, but, as has been pointed out in an excellent recent review (35) of the literature of the dyeing of cellulose with direct dyes, "it is only since 1933 that the investigations have been placed on a sound experimental basis." Prior to 1931 satisfactory rapid methods for the purification of commercial direct dyestuffs were not available, and, also, in many of the early studies the distinction between equilibrium dyeing and the rate of attainment of equilibrium was not always clearly made. Within about the last decade, however, a number of valuable studies, for example, of the effect of temperature and inorganic electrolytes on the equilibrium dye sorption and the rate of its attainment, and of the diffusion coefficients of direct dyes in water and into cellulose have been carried out using purified dyes, and important contributions relative to the mechanism of the dyeing process have been published (see, for example, the review papers by Standing (35), Boulton and Morton (2), and Neale (21) and recent papers by these

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workers and their collaborators). Most of the careful experimental work with cellulosic material has been carried out using regenerated cellulose—viscose yarn or viscose (cellophane) sheet.

In recent years some work involving the interaction of direct dyes and cotton has been reported, viz., comparisons of equilibrium dye sorption on bleached cotton cloth with that on viscose sheet (6, 8, 10, 21, 26) and on other forms of cellulose (10, 25), the effect of salt concentration on the equilibrium sorption of dyes on bleached cotton cloth and other cellulosic materials (6, 10, 26), studies of equilibrium dye sorption on bleached cotton cloth from a mixed dye-bath (28) and on cotton yarn previously dyed with a vat dye (27), a comparison of the rate and extent of dye sorption on cotton hairs and viscose yarn (2), the effect of temperature on the equilibrium sorption of certain direct dyes on cotton (6, 12), the effect of the ash content of cotton on its dye sorption (12), the dependence of certain dyeing properties on the source of the cotton (37), and the desorption of direct dyes from cotton (11, 13, 14, 32, 40). The comment was made (2) in 1940 that "the investigation of the natural cellulosic fibres, cotton, mercerized cotton . . . ., along the lines which have proved so fruitful with regenerated cellulose, has been surprisingly neglected"; only a portion of the aforementioned work with cotton has appeared since this view was expressed, and the statement remains essentially true in 1946.*

In the present work, the dyeing of natural cotton yarn has been studied using a purified blue direct dye. The effects on the equilibrium sorption of dye and the rate of its attainment of varying the temperature of dyeing, of varying the dye concentration, and of adding an anionic surface-active agent to the dye-bath, have been studied.

Surface-active agents are widely used as dye-bath assistants in the direct dyeing of cotton; their use has been recommended, for example, to facilitate the 'wetting-out' of cotton in the dye-bath and to promote level dyeing. The effect of anionic surface-active agents on the sorption of direct dyes by cellulosic material has received, as will be noted later, only scant attention.

Materials and Methods

Cotton

Natural cotton yarn of uniform quality was obtained from Canadian Cottons Ltd., Hamilton, Ont.; the yarn was $\frac{1}{4}$'s count wound on Franklin springs in 14 oz. packages.

For experimental dyeings, the cotton yarn was wound, using a miniature mechanical skein winder, into skeins weighing approximately 5.5 gm., dried at 110° C. (15, pp. 462-464) for 24 hr. (constant weight was attained at this temperature in roughly half this time), and cooled in a desiccator over phosphorus pentoxide. The sample of yarn was weighed rapidly, and sufficient

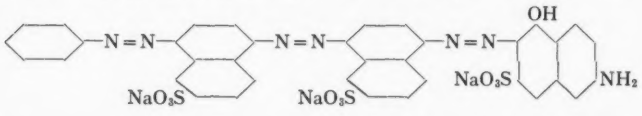
** It has been pointed out (20) that the interpretation of dyeing experiments with cotton yarns is more difficult than the interpretation of those in which viscose sheet is used because of the embedding of the fibres in yarn.*

cut from the skein to bring the weight to about 5.02 gm. The yarn was then dried for a further six hours at 110° C., cooled as before, weighed rapidly, and the weight adjusted to 5.000 ± 0.002 gm. by cutting. Such a procedure was adopted in order to obtain an accurate dry weight.

Before being dyed, the weighed dry cotton skein was allowed to stand in air for 24 hr. to permit regain of moisture (15, pp. 462-464). The dry cotton yarn was found to be appreciably hygroscopic (the 'normal' moisture content will, of course, depend on the temperature and the relative humidity of the air).

Dyestuff

Calcodur Blue 4GL, after purification, was used as the dye throughout this work. This dye (Colour Index 533) is the sodium salt of benzene-azo-6-sulpho-α-naphthalene-azo-6-sulpho-α-naphthalene-azo-6-amino-1-naphthol-3-sulphonic acid ($C_{36}H_{22}N_7O_{10}S_3Na_3$, molecular weight: 877.8). The formula is:



The commercial dyestuff was purified in batches, by the following procedure, the principle of which is due to Rose (30). Forty grams of the commercial dyestuff was dissolved in a minimum quantity of hot (95° to 100° C.) water, and the solution filtered while hot. The hot filtrate was added to one litre of a solution containing 24 gm. of di-*o*-tolylguanidine (Eastman Kodak product) and 25 ml. of 12 *M* hydrochloric acid. The mixture was allowed to cool, and the heavy dark precipitate was filtered and washed repeatedly with water. After the filter cake had been sucked to 'dryness' it was dissolved in methanol (synthetic, 99.85%), and to this solution was added a quantity of a 2 *M* solution of sodium hydroxide in methanol calculated to be sufficient to precipitate (as the sodium salt) about half the dye present. After two days, the precipitated dye was filtered, washed with methanol, dried at 110° C., and ground to a fine powder. The several batches were thoroughly mixed. Before preparing solutions, the dye was dried in an oven at 110° C. for 24 hr., and cooled in a desiccator over phosphorus pentoxide (the purified dye was appreciably hygroscopic, as were also other direct dyes (22)).

The absorption spectrum of the purified dye (in the range 350 to 650 mμ) was detectably different from that of the commercial dyestuff, but subjection of a batch of purified dye to a second similar purification procedure did not result in any further change in the absorption spectrum. The spectrum of a partially exhausted (using cotton yarn) dye-bath solution was compared with that of a dye solution diluted to approximately the same concentration as the partially exhausted bath, and the two found to be almost identical. This may be taken to mean (21, 35) that the purified dye was essentially free from any coloured impurities differing in their substantivity on cotton from that of the main dye.

By means of spectrophotometric tests, aqueous solutions of the dye stored in soft-glass and in Pyrex containers, in diffuse and in direct sunlight and in the dark, were found to be stable, at least over a period of one week (solutions tested daily). Another dye solution, stored in diffuse sunlight indoors, was examined in the spectrophotometer every few hours for a period of two days; no evidence of instability was found.

Surface-active Agents

A representative group of anionic surface-active agents were obtained through the courtesy of a number of industrial concerns. Some of these products were stated by the manufacturer to be 100% 'active'; others were stated to contain various amounts of inorganic salts (commonly sodium sulphate).

As stated below, certain experiments were carried out with the commercial surface-active products; in others, samples purified by a methanol extraction process (31) were used. The extraction process was performed as follows. The product was treated in a Soxhlet extraction apparatus with methanol until the solvent siphoning from the extractor appeared colourless. The methanol solution of surface-active agent was then evaporated to about one-quarter of its volume and cooled, whereupon, in most cases, the agent crystallized from the solution. The crystallized product was dried in air at 110° C. The amount of material remaining in the thimble of the extractor varied from 0 to 65% of the weight of commercial product taken.

Dyeing Apparatus

The dye-pots were constructed from three-necked Woulff bottles of one litre capacity. Each bottle was cut in two (the cut was made about 1 in. below the necks, well above the line of the dye-bath solution) to allow the insertion of a stirrer; the cut edges were ground smooth to ensure a tight fit when sealed with cellulose tape and held together in a suitable clamping frame. The shaft of the stirrer operated through a sleeve arrangement in the centre neck of the flask; in one of the outer necks there was inserted a snug-fitting 'cold-finger' condenser, and in the other a ground glass plug that could be removed when samples of the dye liquor were taken for analysis.

Attention has been drawn by other workers (10) to the importance of suitable agitation of yarn in the dye-bath. The following design of stirrer was adopted after considerable experimentation: the shaft was of 6 mm. glass rod to which were attached, at the end, eight radiating spokes 30 mm. long of 6 mm. glass rod, with the terminals of alternate spokes formed into eyelets. The skein of cotton yarn was suspended beneath this circular stirring head by means of four pieces of platinum wire (B. & S. No. 28) attached at one end to the glass eyelet and at the other to the centre of the shaft. This stirrer was given an up and down motion (stroke of 3 cm. and period of 1 sec.) in the dye-bath solution by means of an electromagnetic plunger-action device described elsewhere (38). This stirring device was found to give excellent results with respect to levelness of dyeing and reproducibility of results.

The dye-pots, equipped with requisite stirrers and condensers, were immersed in a constant temperature bath insulated so as to be capable of operation in the range 15° to 99° C., and equipped with a thermoregulator permitting temperature control to ± 0.1° C. of the desired temperature.

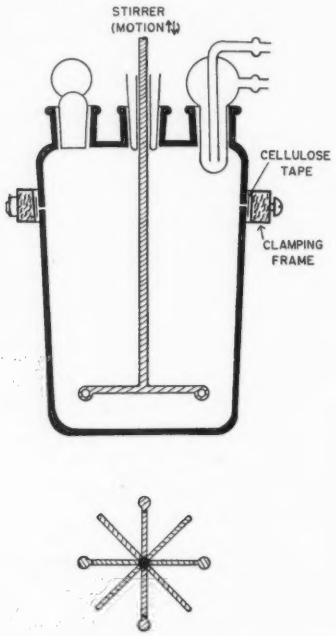


FIG. 1. *Side view of dyeing apparatus (in full section) with bottom view of stirrer head shown underneath.*

Dyeing Procedure

In all dyeings reported in this paper, 5.000 ± 0.002 gm. (dry weight) of cotton yarn was dyed using 250 ml. of dye solution. The dye solution, which always contained 4.00 gm. per litre of sodium chloride (analysed grade), varied in its initial concentration from 10.0 to 45.5 mgm. per litre (1.1×10^{-5} to 5.2×10^{-5} *M*).*

The assembled dye-pot, with the skein of cotton yarn in place, but not containing the dye-bath solution, was placed in the constant temperature bath and allowed to come to the appropriate temperature. In a Pyrex bottle, also contained in the bath, a solution containing dye, sodium chloride (and possibly a surface-active agent), at appropriate concentrations was brought to temperature. Using a pipette, 250 ml. of the dye-bath solution was removed

* *Concentrations of dye-bath components are frequently expressed in terms of the weight of material being dyed. In these terms, the liquor-to-yarn ratio was 50 : 1, the salt concentration was 20%, and the dye concentration varied from 0.05 to 0.23%.*

from the bottle, added to the dye-bath through the neck normally stoppered with a glass plug, and the stirrer and timer started.

At appropriately spaced intervals, small (5 ml.) samples of the dye-bath solution were removed through the neck of the dye-bath normally stoppered, cooled to room temperature, analysed spectrophotometrically (*vide infra*) for dye content, and then replaced in the dye-pot.

Measurement of Dye Concentration

Unknown concentrations of dye in solution were determined using a Coleman Model 11 Universal spectrophotometer, equipped with the 'PC-4' filter; matched rectangular cuvettes, with a path length of 5 mm., were employed. The reference cuvette contained distilled water. Calibration of the instrument (at a setting of 600 mμ, a maximum in the absorption spectrum) was effected at room temperature using dye solutions of known concentration (assuming that the dye was dry after heating in air for 24 hr. at 110° C.) and containing sodium chloride in the same concentration (4.00 gm. per litre) as used in dyeing experiments. The presence of the salt noticeably affected the spectrum—for example, changing the maximum from 610 to 600 mμ. Experiments showed that the transmittance (at least over the range 525 to 625 mμ) of a dye solution containing sodium chloride (4.00 gm. per litre) was not measurably affected, at room temperature, by the presence of surface-active agents in the concentrations encountered in this work.

A plot of the dye concentration against the logarithm of the per cent transmittance yielded a straight line, either in the presence or absence of sodium chloride (4.00 gm. per litre) with dye concentrations at least as high as 50 mgm. per litre (5.7×10^{-5} *M*). This conformity with Beer's law would indicate that, at least up to this concentration, either the dye was not aggregated or else that the extent and nature of the aggregation remained constant.

From the concentration of dye remaining in the dye-bath liquor t minutes after the start of dyeing and the concentration of dye in the liquor before its contact with cotton (likewise determined with reference to the spectrophotometric calibration curve), the sorption* of dye on the cotton at time t may, of course, be readily calculated. Dye sorptions reported below are calculated in terms of milligrams of dye sorbed per 100 gm. of cotton yarn (dry weight). In the experiments below, surface-active agents were absent from the dye-bath liquor unless the contrary is stated.

Experimental Results

Variation in Initial Dye Concentration

A series of dyeings was carried out at 90° C. with the initial concentration of dye in the dye-bath solution varying from 10.0 to 45.5 mgm. per litre.

* *Several workers (e.g., Neale, Boulton, and Standing) refer to the 'absorption' of direct dyes by or on cellulosic material. The term 'adsorption' is also sometimes employed. Inasmuch as these terms are used in different senses by different authors (see, for example, Thomas (36, pp. 272-273)), the present writers prefer the use of the non-committal term 'sorption' (17, 18).*

The dye sorption as a function of time of dyeing is plotted in Fig. 2. The dyeing at an initial dye concentration of 20.0 mgm. per litre was carried out in duplicate; the results obtained (as well as data secured from other experiments) showed that the equilibrium sorption value was reproducible with a precision of within 1%.

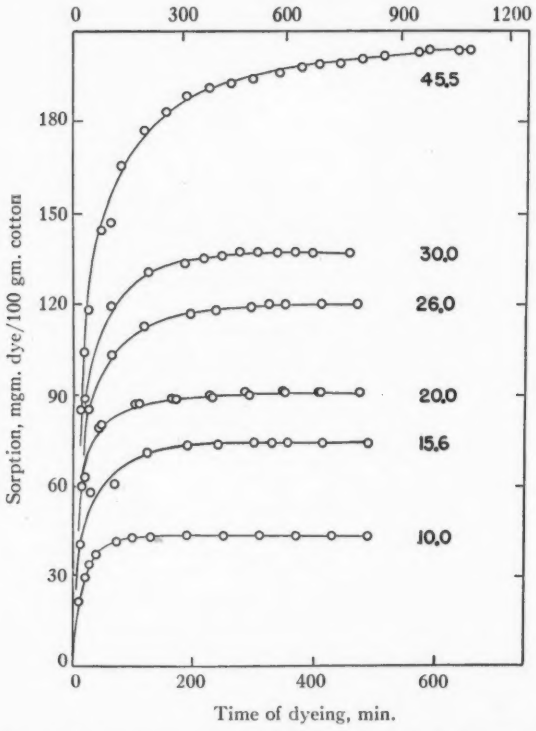


FIG. 2. *Effect of dye concentration on the equilibrium sorption and the rate of its attainment at 90° C. (The figures adjacent to the curves refer to initial dye concentrations in mgm. per litre. The upper time scale applies only to the curve with an initial dye concentration of 45.5 mgm. per litre).*

A plot of the logarithm of the equilibrium sorption value against the logarithm of the final, or equilibrium, concentration of dye in the bath is shown in Fig. 3, and a plot of the equilibrium sorption value against the initial concentration of dye in the dye-bath is given in Fig. 4.

Variation in Temperature

A number of dyeings were carried out, over a range of temperature, with an initial dye concentration of 26.7 mgm. per litre. The resultant data are plotted in Fig. 5.

Sorption–time curves were also obtained at 80° and 90° C. for dyeings in which the initial dye concentration was 20.0 mgm. per litre. The data obtained in these runs are plotted semilogarithmetically in Fig. 6.

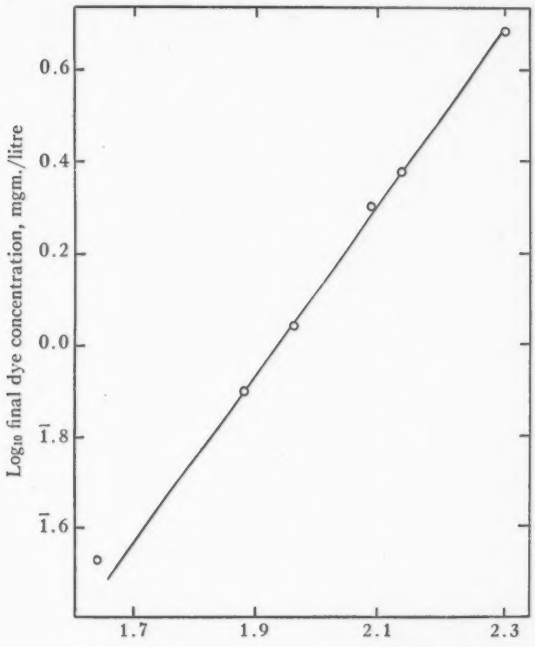


FIG. 3. *Relation of equilbrium sorption at 90° C. to equilibrium concentration of dye in the bath. (Data obtained from curves of Fig. 2.)*

Presence of Anionic Surface-active Agents

In Table I there are given the composition of the anionic surface-active agents tested, the percentage of surface-active material stated by the supplier to be present in each case, and the designations used later in the paper in referring to the agents.

Dyeing experiments were carried out at a temperature of 60° C., using an initial dye concentration of 26.7 mgm. per litre, with an anionic surface-active agent present in the dye-bath liquor at a concentration of 0.200 gm. per litre (1%, based on the weight of cotton yarn). In most of these experiments the dye sorption was measured over only the first two hours of the dyeing process.

The effect on the rate of dyeing, in the early stages of the dyeing operation, of the presence of surface-active agents is shown in Fig. 7. The heavy line in this figure is for a dyeing at 60° C. under similar conditions but in the absence of a surface-active agent, and the dotted line is for a comparable dyeing at

90° C. in the absence of surface-active agent. In order to eliminate crowding on the graph, the data for certain of the agents have not been plotted. The

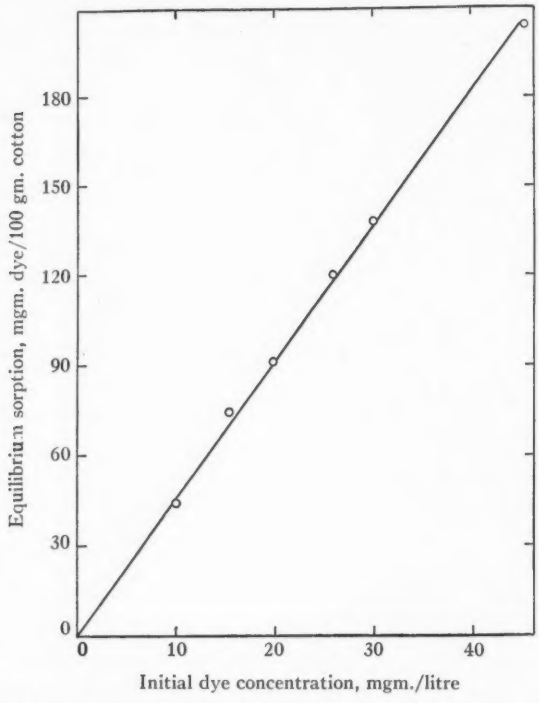


FIG. 4. *Relation of equilibrium sorption at 90° C. to initial concentration of dye in the bath. (Data obtained from curves of Fig. 2.)*

TABLE I

ANIONIC SURFACE-ACTIVE AGENTS USED

Nature of agent	Active material, %	Designation
Monobutyl phenyl phenol sodium monosulphonate	100	*A*
Dibutyl phenyl phenol sodium disulphonate	100	*B*
Decylbenzene sodium sulphonate	100	*C*
Dodecylbenzene sodium sulphonate	100	*D*
An alkyl (long chain) aryl sodium sulphonate	90*	*E*
An alkyl (long chain) aryl sodium sulphonate	40*	*F*
Disodium tri-isobutenyl succinate	100	*G*
Dioctyl sodium sulphosuccinate	100	*H*
Sodium salt of sulphated monoglycerides from coconut oil	98**	*I*
Sodium salt of sulphated monoglycerides from coconut oil	35**	*J*

* *Remainder stated to be inorganic salts, chiefly sodium sulphate.*

** *Remainder stated to be sodium sulphate.*

curve for agent *C* fell almost on top of that for agent *E*, i.e., somewhat above that for the corresponding dodecyl compound, *D*. The curve for agent *B*

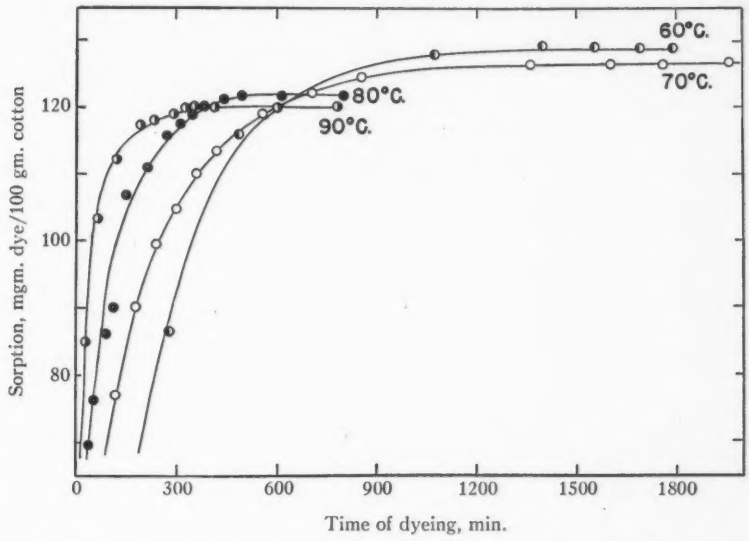


FIG. 5. *Effect of temperature on the equilibrium sorption and the rate of its attainment.*

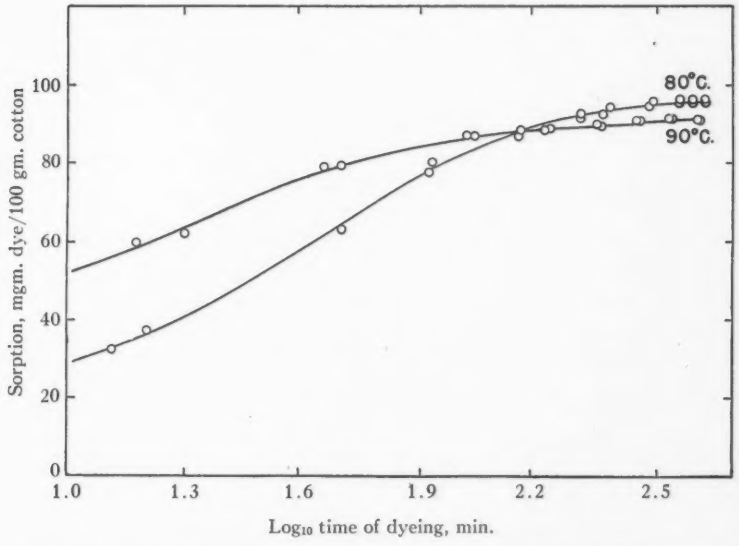


FIG. 6. *Effect of temperature on the equilibrium sorption and the rate of its attainment.*

fell below that of agent *D* and above that for the related monobutyl compound, *A*. The curve for agent *F* fell below that of the related agent *E*, close to that for *D*. Agent *G* was unique among the compounds investigated, in that it appeared to exert a slight rate-depressing effect.

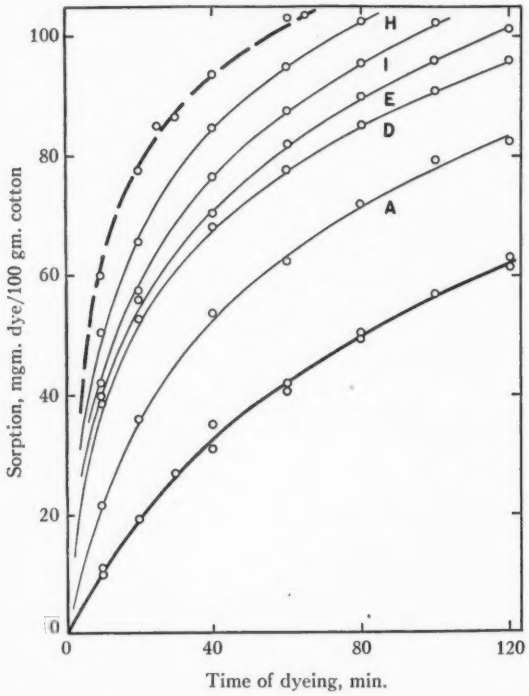


FIG. 7. *Effect of commercial anionic surface-active agents on the rate of sorption at 60° C. (The heavy solid line is for a dyeing at 60° C., and the dotted line for one at 90° C., in the absence of surface-active agent.)*

In Fig. 8 are plotted curves obtained from similar experiments, but in which methanol-soluble fractions of the surface-active agents were used, rather than the commercial products. The heavy and dotted lines in this graph have the same significance as in Fig. 7. Although the data are not plotted, it was found again that the curve for agent *C* lay slightly above that for agent *D*.

The effect of the purity of the agent is shown in Fig. 9. Curve 1 was obtained in the absence of surface-active agent, Curve 2 with the methanol-soluble fraction of agent *I*, Curve 3 with agent *J* and Curve 4 with agent *I* (all surface-active agents at a concentration of 0.200 gm. per litre).

The activity of the surface-active agent as a function of its concentration is shown in Fig. 10. Curve 1 was obtained in the absence of surface-active agent, Curve 2 with surface-active agent *F* (commercial) at a concentration

of 0.040 gm. per litre, Curve 3 with the agent at a concentration of 0.100 gm. per litre, Curve 4 with a concentration of 0.200 gm. per litre, and Curve 5 with a concentration of 0.500 and 1.000 gm. per litre.

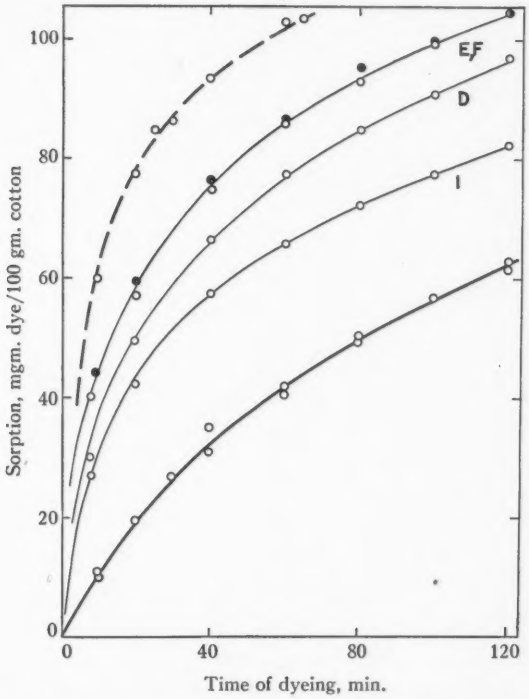


FIG. 8. *Effect of purified anionic surface-active agent on the rate of sorption at 60° C.*

Similar results were obtained using the methanol-soluble fraction of agent *I*; here again, the points for a concentration of 0.500 and 1.000 gm. per litre lay on the same curve.

The effect of a surface-active agent on the extent of dye sorption at equilibrium, as well as on the rate of sorption, is clear from Fig. 11, in which Curve 1 relates to a dyeing at 70° C. with an initial dye concentration of 26.7 mgm. per litre but with no surface-active agent present, and Curve 2 is for a dyeing under similar conditions but with the methanol-soluble fraction of agent *E* present in the dye-bath liquor at a concentration of 0.200 gm. per litre.

A similar pair of curves was obtained under the same conditions except for the use of a temperature of 60° C. At this temperature the effect of the surface-active agent on the equilibrium sorption (and on the rate of sorption) was somewhat more pronounced than at 70° C.; on the other hand, similar experiments at a temperature of 80° and 90° C. showed that the effect of the

surface-active agent on the equilibrium sorption was not detectable at these temperatures (although the effect on the rate was still observable at 80° C.).

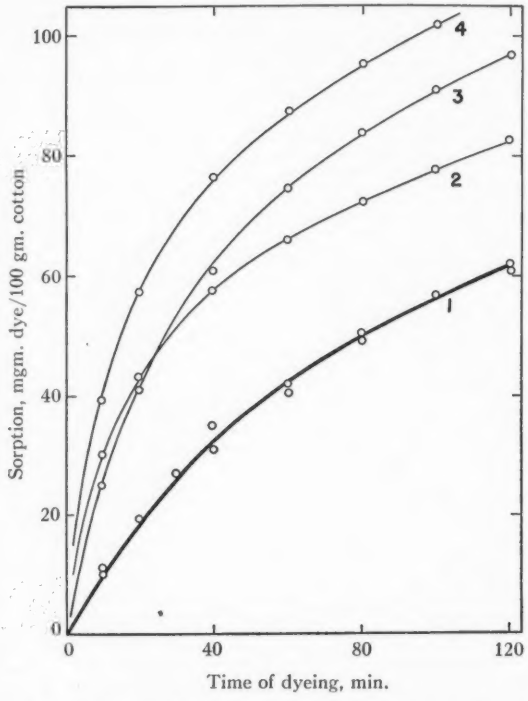


FIG. 9. *Effect of purity of a surface-active agent on its activity at 60° C.*

Discussion

It is evident from Figs. 2, 5, and 11 that the sorption of dye is relatively rapid during the early stages of the dyeing operation, but that the rate of dyeing decreases steadily as saturation, or the equilibrium sorption value, is approached. These dye-sorption–time curves are similar in shape to those that have been obtained during the study of the dyeing of viscose sheet with direct dyes (e.g., 9, 23, 24). The shape of the sorption–time curve is not, *per se*, evidence that any particular process, either chemical or physical, is the rate-controlling factor in the dyeing process.

Effect of Dye Concentration

From Fig. 2 it is clear that the time required to attain equilibrium conditions at 90° C. increases markedly as the initial concentration of dye in the bath is increased (concomitantly, the final or equilibrium concentration of dye in the bath is increased). The rate of dyeing (in terms of milligrams of dye sorbed

per 100 gm. of cotton in unit time), however, increases with increasing concentration of dye. Neale has found that the apparent diffusion coefficient of a direct dye into viscose sheet (determined under conditions of a very low

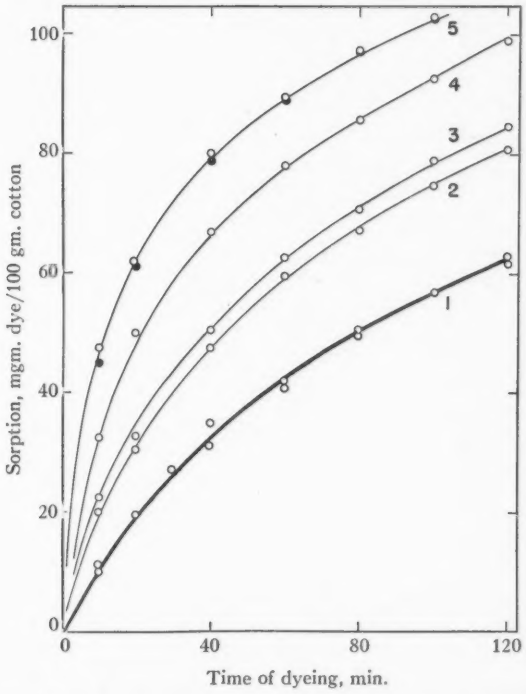


FIG. 10. *Effect of concentration of a surface-active agent on its activity at 60° C.*

degree of dye-bath exhaustion at equilibrium, rather than a very high degree as in the present experiments) increased as the concentration of dye in the bath increased (21), and that the diffusion coefficient of the dye increased with the concentration of absorbed dye (7).

An increase in the equilibrium sorption of direct dyes with increasing concentration of dye in the bath has been observed in the dyeing of viscose sheet (9, 24) and bleached cotton cloth (10), and the relation between sorption on viscose sheet and dye concentration found (7, 23, 41) to be expressible by a Freundlich equation.* That this equation represents the relation existing between the equilibrium sorption of Calcodur Blue 4GL on natural cotton

* $a = Kc^n$, *where* 'a' = *amount of solute sorbed by a given mass of sorbent at equilibrium,* 'c' = *equilibrium concentration of solute in the solution, and* 'K' *and* 'n' *are constants. The equation is that of a 'generalized' parabola; log* 'a' *varies linearly with log* 'c' *(e.g., Fig. 3). McBain has noted (19, p. 5) that it is very incorrect to attribute this equation to Freundlich, as is commonly done.*

yarn and the final or equilibrium concentration of dye in the solution is clear from Fig. 3. The applicability of this equation does not imply any particular mechanism for the dyeing process; the 'Freundlich' equation is an empirical one—as has been pointed out (29, p. 8), it "is a mathematical expression which will closely represent any chemical or physical phenomenon which proceeds at a diminishing ratio."*

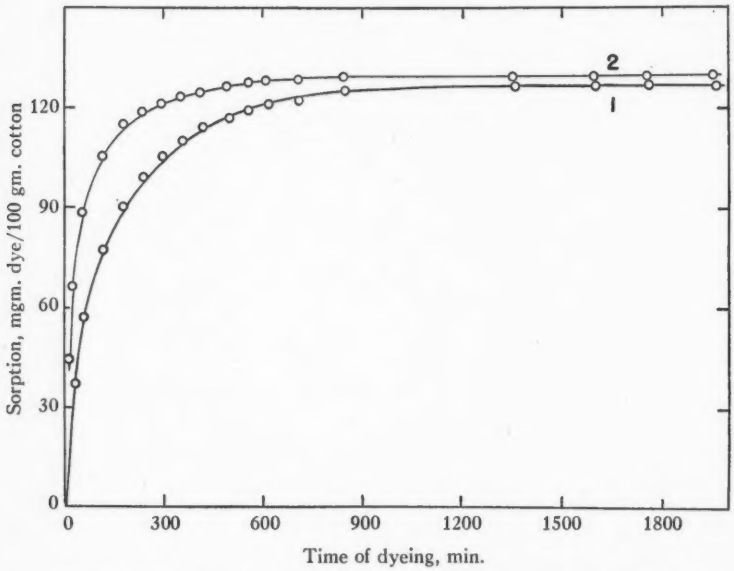


FIG. 11. *Effect of surface-active agent on the equilibrium sorption at 70° C.*

Fig. 4 shows that the relation between the equilibrium sorption value and the initial, rather than final, dye-bath concentration is a linear one, at least over the range of dye concentration studied. Because the ratio of the mass of dye liquor to that of cotton yarn was maintained constant, this linearity implies that the fraction of the dye initially present that is sorbed at equilibrium (or the degree of dye-bath exhaustion at equilibrium) is, in the present experiments, essentially independent of the initial dye concentration. This phenomenon, to which attention does not appear to have been drawn in the literature of the dyeing of cellulosic materials with direct dyes, would very likely be observable only under conditions leading to relatively high dye-bath exhaustions; in the experiments under consideration the exhaustions were all close to 92%. In experiments on the dyeing of cuprammonium yarn with direct dyes it has been shown (1) that the exhaustion of the dye-bath may

* *It should be mentioned that a recently proposed theory of dyeing predicts (41) that the sorption isotherms, at constant salt concentration, will take the form of the 'Freundlich' equation.*

decrease from close to 100 to below 20% when the initial dye-bath concentration is increased approximately 100-fold. It should be mentioned that in relatively recent work on the dyeing of viscose sheet with direct dyes (e.g., that by Neale and his co-workers to which reference has and will be made) the conditions of dyeing were so chosen that the decrease in the concentration of dye in the bath during dyeing was very slight (usually less than 2%). Such a technique facilitates theoretical interpretation, but it is, of course, far removed from commercial practice.

Effect of Temperature

It has been shown (6, 23) that when viscose sheet is dyed with direct dyes an increase in the temperature decreases the equilibrium sorption of dye but increases the rate of attainment of equilibrium; these effects of temperature are, of course, common to many types of sorption phenomena. That they are evidenced in the direct dyeing of natural cotton yarn is shown in Figs. 5 and 6. The sorption–time curves plotted with a logarithmetic time scale (Fig. 6) are similar in shape to those that have been obtained for viscose rayon yarn (1, 2) and for cotton hairs (2). It should be noted that it has been found (6) that the equilibrium sorption of certain direct dyes on bleached cotton cloth is decreased by an increase in temperature; but a case has been reported (12) in which equilibrium dye sorption (on absorbent surgical cotton) increased with an increase in temperature.

A decrease in the value of the equilibrium sorption of Calcodur Blue 4GL on natural cotton with increasing temperature means that the dyeing process is an exothermic one. The heat of dyeing of cellulosic material with direct dyes would appear to have been assessed for only two dyes (16, p. 274; 41), and these determinations were made from the temperature coefficient of the equilibrium sorption on viscose sheet. It is planned to undertake in this laboratory an investigation of the heats of dyeing of natural cotton yarn by a number of direct dyes.

Effect of Anionic Surface-active Agents

The rate of direct dyeing of mercerized cotton yarn at room temperature has been shown (4, 31) to be accelerated in the presence of certain anionic surface-active agents. On the other hand, the rate of dyeing of cotton pongee with a direct dye at 25° C. in the presence of a number of anionic surface-active agents has been shown (32) to be either increased or decreased (at least during the first hour of the dyeing process), depending on the concentration of sodium chloride present. From Figs. 7-11 it is evident that anionic surface-active agents of the sulphonate (either alkyl aryl or aliphatic) type and sulphated aliphatic esters accelerate the rate of sorption of Calcodur Blue 4GL on natural cotton yarn in the presence of sodium chloride (4.00 gm. per litre). The statement by Snell (34) that "an anion-active agent added to a bath containing acid dye, since each gives a large negatively charged ion, slows

down the sorption according to the amount of agent added" cannot, therefore, be accepted.

In some cases the rate-accelerating effect obtained at 60° C. due to the addition to the dye-bath of 0.2 gm. per litre of a surface-active agent is almost equivalent to that obtained by raising the temperature, in the absence of a surface-active agent, to 90° C. (e.g., see Fig. 7). All the surface-active agents showing a positive effect on the rate at 60° C. were more effective (at a concentration of 0.2 gm. per litre and, in at least one case, at a tenth of this concentration) than raising the temperature 10° C., in the absence of a surface-active agent.

A comparison of Figs. 7 and 8 shows that the methanol-soluble fraction of agent *D* has essentially the same activity as the commercial product, whereas the methanol-soluble fraction of agent *I* has a significantly reduced activity; this reduction in activity is shown more obviously in Fig. 9. The data plotted in Fig. 9 show that the effect of commercial surface-active agents on the rate of sorption is not due, or at least not largely due, to the presence of inorganic salts in the surface-active preparations because agent *I*, which is 98% 'active,' has a significantly greater effect than agent *J*, which is 35% 'active' (the remainder is stated to be sodium sulphate). The methanol-soluble fraction of agent *I* has a smaller effect on the rate than the unpurified agent *I* presumably because that fraction of the surface-active material present that is soluble in methanol is rather less 'active' than the fraction of surface-active material that is not extracted by methanol. The reduction in the rate-accelerating effect of a surface-active preparation due to the presence of inorganic salts is again evidenced in the data obtained with agents *F* and *E*. It has been noted that the rate-accelerating effect of agent *E* (90% 'active') is greater than that of agent *F* (40% 'active'), and consideration of Figs. 7 and 8 will show that the methanol-soluble fractions of these agents not only exhibit the same activity, but an activity greater than that of the commercial agent *E*.

The dependence of the rate-accelerating effect of a surface-active agent on its concentration is shown in Fig. 10. With this agent (*E*) the maximum rate effect, at least in so far as the early stages of the dyeing process are concerned, is achieved at a concentration of 0.5% or less (but greater than 0.2%); a similar result was found for the methanol-soluble fraction of a different agent (*I*), as noted earlier.

It is the authors' view that anionic surface-active agents exert their effect by virtue of an ability to promote wetting and swelling of the cotton fibres. These physical effects would result in an increased rate of sorption, as has been found in this work. Once the available cellulosic surface is saturated with surface-active agent (oriented with the polar or hydrophilic group facing the aqueous phase), an increase in the concentration of the latter would have

no effect; this optimal value for the concentration of surface-active agent has been observed (Fig. 10). In Fig. 11 it is shown that the presence of a surface-active agent may result in an increased value for the equilibrium sorption. This phenomenon, apparently not previously observed, is understandable, and to be expected, if an action of the surface-active agent is to increase the swelling of the fibre, thus increasing the capillary dimensions and/or making available minute channels and intermicellar spaces that would not have been available for dye penetration in the absence of the surface-active agent; the latter, in this sense, creates additional surface upon which dye may be sorbed.

It has been noted in the section dealing with experimental results that the activity of an anionic surface-active agent (purified agent *E*) decreases, both as regards effect on the equilibrium sorption and the rate of its attainment, as the temperature is increased. This effect may be due to a decrease, with increasing temperature, of the wetting ability of this surface-active agent. Although it is, perhaps, more common for the wetting power* of an anionic surface-active agent to increase as the temperature is raised, the effect of temperature on this property is variable (3, 5); a case has been reported (3), for example, in which the wetting power (measured by the Draves test using a skein of gray cotton yarn) of an anionic surface-active agent goes through a maximum as the temperature is raised and then falls off rapidly at temperatures above 55° C.

It was noted earlier that spectrophotometric tests showed that the surface-active agents had no appreciable effect on the absorption spectrum of the dye in the presence of salt. If the effect of the surface-active agent did not arise, as suggested above, through an action on the fibre, but as a result of changing the degree of aggregation or association of the dye, then one would expect to find evidence of this in the spectrophotometric work†, although this work was carried out at room temperature and the dyeings were at an elevated temperature (the aggregation of dyes decreases with increased temperature (2, 32, 35)). The effect of surface-active agents on particle size of dye micelles has been inferred from their effect on the aqueous diffusion coefficient of the dye (32, 35, but cf. 20). A few investigations of this nature have been carried out, and reviewed by Standing (35); some surface-active agents, such as certain cationic ones, very appreciably reduce the diffusion coefficient‡ (and thus, presumably, greatly increase the aggregation of the dye micelles), whereas the anionic surface-active agents investigated affected the aqueous diffusion

** Snell has pointed out (34) that "the term 'wetting power' is variously used as meaning the process of wetting, the degree of wetting, the ease of wetting, or the speed of wetting." Both the Herbig and Draves tests primarily measure speed of wetting.*

† β-naphthol, which is sometimes used as a levelling agent for direct dyes, has been found (28) to have no effect on the spectrum of Chlorazol Sky Blue FF, nor, at the concentration used, on its 'absorption' by bleached Egyptian cotton cloth. On the other hand, β-naphthol has been reported to increase the speed of dyeing (1, 2) and decrease the dye sorption (2) in some cases.

‡ Cationic surface-active agents are employed as levelling agents in the direct dyeing of cotton, and it has been suggested (33) that they function as such by their action as retardents for the dyeing rate.

of the dye only slightly. This constitutes further evidence that anionic surface-active agents exert their effect primarily not through an action on the dye, but as a result of one involving the fibre (32, 33, 39).

Acknowledgments

The authors wish to express their appreciation to Canadian Cottons Ltd., Montreal, for the financial support given to this work. One of the authors (W. J. S.) is also indebted to the National Research Council of Canada for the award of a Bursary, which made it possible for him to undertake this study.

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RESIN–RUBBER FROM CANADIAN GROWN PLANTS

VI. PEBBLE-MILLING MILKWEED LEAVES IN CLOSED CIRCUIT[1]

By R. V. Tomkins[2] and N. H. Grace[3]

Abstract

Conversion from batch to closed-circuit continuous operation increased the capacity of a pebble-mill from 5 to 14.5 lb. solids per hour when grinding digested milkweed leaves to pass 60 mesh for subsequent separation of resin–rubber by froth flotation. The rate of grind is a decreasing function with time in the mill; this indicates use of large mill discharge and recycle rates for high capacity.

Introduction

Attention has recently been given to milkweed leaves as a source of a resin–rubber gum for blending with GR–S, and a pilot plant process consisting of digestion, pebble-milling, froth flotation, and recovery from the concentrate has been described (1). The pebble-milling operation was performed batchwise and its conversion to closed-circuit continuous milling appeared desirable since the limiting factor of the batch process was the capacity of the pebble-mill. Continuous operation should increase the capacity of the mill and reduce labour requirements, which were the major cost factors in batch milling.

Also, continuous closed-circuit milling has the advantage of removal of the ground product as soon as, or shortly after, it has reached the desired size. This eliminates overgrinding and, in this instance, minimizes the tendency of the cellulosic material to gelatinize or swell as a result of prolonged milling. The capacity of the mill when used batchwise was 15 to 20 lb. of solids for each 3.5 hr. milling period, or approximately 5 lb. of solids per hour. If even this rate could be achieved by continuous operation, the time and labour necessary for loading, draining, and screening would be eliminated.

This investigation included determination of a typical batch grinding rate, preliminary continuous runs to check operation of equipment under various feed conditions, and final runs for determination of capacity obtainable with the auxiliary equipment available. As the product was not in demand, and the supply of milkweed leaves limited, the aim of this work was the determination of the practicability of such continuous milling rather than a detailed study of the various operations. However, the information obtained may be of use for the development of similar milling processes, as literature on this type of operation is rather meagre.

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[3] *Biochemist, Industrial Utilization Investigations.*

Equipment

The units comprising the milling circuit are shown in their relative positions in Fig. 1. The digested milkweed leaves (1) were fed by a screw conveyor through a hollow trunnion of the pebble-mill and discharged through the other trunnion to the vibrating screen. The oversize flowed into the boot of the bucket elevator, which returned it to the feed end of the mill for further grinding. The undersize was pumped to a calibrated storage box for subsequent froth flotation.

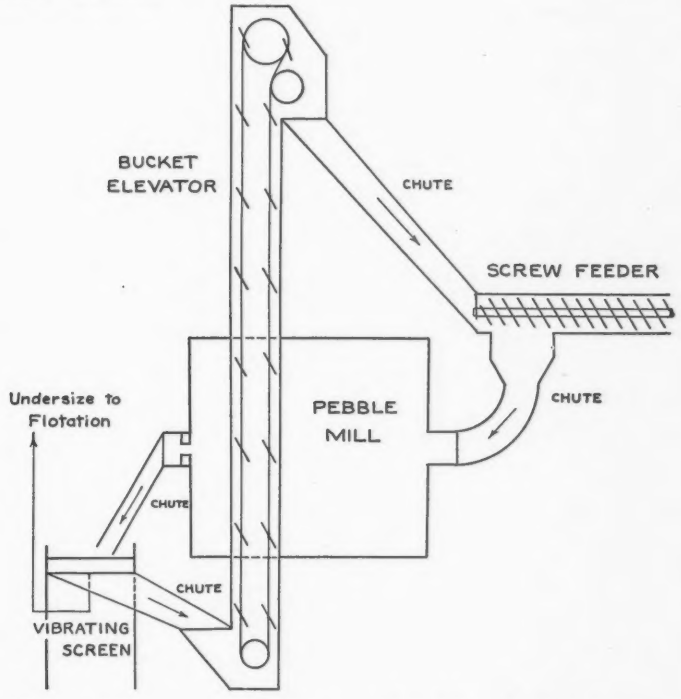

FIG. 1. *Milling circuit for continuous grinding of digested milkweed leaves.*

Feeder

An open spiral conveyor with a 4 in. diameter screw rotating at 1.5 r.p.m. fed the digested leaves to the pebble-mill. The feeder served to smooth the flow, rather than to meter the feed, which was weighed and brought to the desired consistency before being placed in the conveyor.

Pebble Mill

A Straub mill, 36 in. diameter by 36 in. long, gross capacity 130 gal., lined with porcelain brick was used to comminute the digested leaves. Flint pebbles (average diameter, 2.3 in.) occupied about 25% of the gross volume.

The mill was rotated at 32 r.p.m. (80% of theoretical critical speed). The feed was admitted through a metal chute attached to the bearing housing to a hollow trunnion having a 6 in. diameter opening. The discharge end was fitted with a wooden plug containing a hole 2 in. in diameter, small enough to prevent the pebbles from leaving the mill.

Vibrating Screen

The ground material was carried by an open chute from the mill to a Dillon vibrating screen. The screen used was 60 mesh stainless steel, 18 by 48 in., oscillating about 30 times per sec. and sloped 5° to the horizontal.

Bucket Elevator

The elevator carried 16 buckets of 28 cu. in. capacity, travelling 75 ft. per min., thus having a maximum capacity of 2700 lb. per hr. of the oversize material. The lift was about 10 ft., allowing the material to flow by gravity back to the mill.

Experimental Procedure and Results

The milkweed leaves used throughout this investigation were prepared by digestion and washing as previously described for batch milling (1).

Moisture determinations were made by drying at 105° C. for 48 hr. Resin–rubber contents were obtained by successive 24-hr. acetone and benzene extractions (2).

Batch Milling

At various times during a batch run 20-lb. samples of slurry were removed and passed over the vibrating screen. The oversize was collected and weighed, and solid content of the mill slurry and the oversize determined. In addition a 20 lb. sample of unmilled material was screened. The solid content of the mill slurry was 5.4%. The points on the curve in Fig. 2 were obtained by calculation from these data.

Although the conditions in the mill during batch operation are somewhat different from those during continuous operation, certain general conclusions may be applied. The instantaneous rate of grind is given by the slope of this curve (Fig. 2) at any point, and, assuming the form of the curve to be typical, the rate is a decreasing function with time, being greatly reduced during the first hour. Therefore it is desirable to have a high discharge rate from the continuous mill, corresponding to a short period of milling per pass, in order to obtain the advantage of the higher rates of grind.

Continuous Milling

The capacity of the system is limited by the rate of grind attained in the mill, but it is possible that the recycle equipment may not be large enough to allow the maximum capacity to be attained.

The consistency of the feed is limited by the minimum solid content desired for flotation (2%) and the solid content of the cooked washed leaves (5 to 7%). Below 2%, thickening would be necessary for satisfactory flotation.

The following balances are applicable if the system is in equilibrium:

Around the whole circuit:

$$F = U \tag{1}$$

$$fF = uU \tag{2}$$

Around the feeder:

$$F + R = M \tag{3}$$

$$fF + rR = mM \tag{4}$$

Around the screen:

$$U + R = M \tag{5}$$

$$uU + rR = mM\,. \tag{6}$$

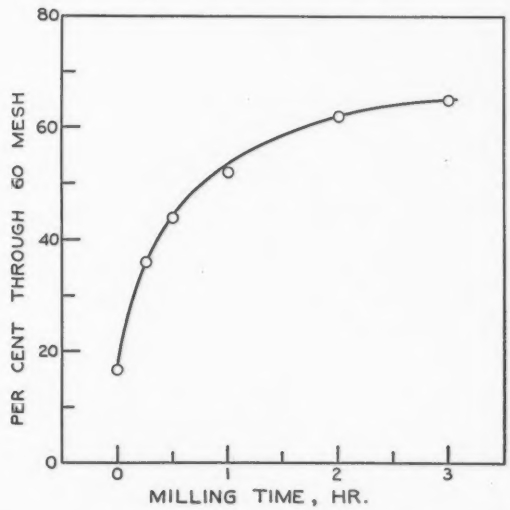

FIG. 2. *Grinding rate on batch milling.*

The fractional solid contents of the feed, undersize, recycle, and mill discharge are represented by f, u, r, m, respectively. The corresponding capitals indicate gross flow rates in pounds per hour.

The test for equilibrium is that Equations (1) and (2) must be satisfied. However, as slight losses are inevitable in the system the criterion that

$$f = u \tag{7}$$

was selected.

The quantities U and F are easily measured, but as R and M are somewhat unsteady owing to slight variations in feed, only approximate values could be obtained during the runs. From (3) and (4) the following equations were obtained:

$$R = \frac{F(m-f)}{(r-m)} \tag{8}$$

$$M = \frac{F(r-f)}{(r-m)}\,. \tag{9}$$

The right-hand values could all be measured, but, as the bracketed factors have very small values, the error in the calculated values may be large. The figures given further on were a compromise between observed and calculated values.

An estimate of the average rate of grind can be made from the following considerations. The fraction of solids going through 60 mesh per pass through the mill is given by

$$K = \frac{uU}{mM} = \frac{fF}{mM} . \tag{10}$$

The mill load is about 350 lb. of slurry. Then the average time (hours) in the mill per pass

$$t = \frac{350}{M} . \tag{11}$$

The average rate of grind, b, is obtained by dividing Equation (10) by Equation (11)

$$b = \frac{K}{t} = \frac{fF \times M}{mM \times 350} = \frac{fF}{350m} . \tag{12}$$

This value gives a rate of grind for comparison with the slope of the curve in Fig. 2.

The procedure for making continuous runs follows. The mill was charged at the desired solid content and run without feed for two hours. Feeding was then begun at the desired rate by placing weighed amounts of leaves of the required solid content in the feeder at 10-min. intervals. Preliminary runs were designed to check equipment operation under various feed conditions. Samples were taken of the undersize four hours after feed started and the solid contents determined to discover whether equilibrium had been established.

Run 1. Feed: 250 lb. per hr. at 2% (5 lb. solids per hr.). Undersize: 1.95% solids, equipment operation satisfactory. Equilibrium established.

Run 2. Feed: 125 lb. per hr. at 4% (5 lb. solids per hr.). Undersize: 3.6% solids, equipment operation satisfactory. Equilibrium not established.

Run 3. Feed: 400 lb. per hr. at 2% (8 lb. solids per hr.). Undersize: 1.9% solids, equipment operation satisfactory. Equilibrium closely approached.

Run 4. Feed: 200 lb. per hr. at 4% (8 lb. solids per hr.). Undersize: 3.5% solids, the screen was somewhat overloaded and mill discharge plugged at intervals by underground material. Equilibrium not established.

This led to the selection of about 2% as the solid content of the feed for final runs. This also gives larger total feed rate (pounds per hour) for a given solid feed rate (pounds of solids per hour), thus possibly resulting in higher mill discharge rates and higher rates of grind. During the final runs,

samples were taken hourly. The feeds contained 2.3% solids. The results from runs at 5.75, 11.5, and 14.5 lb. solids per hr. are given in Table I. In all these millings, equilibrium was established, the minor fluctuations being due to variation in the feed. A run at 17.5 lb. solids per hr. was unsuccessful, as the bucket elevator could not handle the recycle.

TABLE I

CONTINUOUS MILLING RUNS

Feed	Hours run*	Undersize, % solids	Recycle		Mill discharge	
			Lb./hr. (estimated)†	% solids	Lb./hr. (estimated)†	% solids
5.75 lb. solids/hr. (250 lb./hr. at 2.3% solids)	2	1.7		5.3		2.8
	3	1.9		4.5		2.8
	4	2.3		4.6		3.0
	5	2.2	200	4.4	450	3.1
11.5 lb. solids/hr. (500 lb./hr. at 2.3% solids)	2	2.5		4.4		3.8
	3	2.4		4.4		3.5
	4	2.3		4.3		3.9
	5	2.4	1000	4.3	1500	3.9
14.5 lb. solids/hr. (625 lb./hr. at 2.3% solids)	2	2.2		4.0		3.1
	3	2.1		3.9		3.4
	4	2.3		3.7		3.2
	5	2.2	1800	3.8	2425	3.6

* *From beginning of continuous feed.*

† *See text.*

The slurries obtained from these runs were subsequently passed through the froth flotation cell and this operation proceeded as efficiently as when batch-milled material was used. Analyses of the slurries for resin–rubber were compared with the resin–rubber content of the unmilled leaves and were found to be substantially the same; this indicated no accumulation of resin–rubber in the mill.

Table II shows the average values for rates of grind. Although these values are only approximate, they show that, as predicted, the rates of grind increase very appreciably as the time of passage through the mill decreases.

The vibrating screen and elevator do not have enough capacity to match the mill. Higher grinding rates could be obtained with larger recycle equipment, the maximum being attained only when the rate of discharge of the mill has reached its limit, as determined by the size of the discharge opening and viscosity of the slurry. However, the recycle rate increases greatly as feed rate is increased and the necessary equipment would probably be so large as to overshadow any advantage of high milling capacities.

Here, the batch rate has been nearly tripled by continuous operation, and the material appears well suited to closed-circuit milling.

TABLE II

AVERAGE RATES OF GRIND ATTAINED

Feed, lb. solids/hr. (fF)	Mill discharge		k, fraction through 60 mesh per pass	t, hours per pass	$b = k/t$ fraction through 60 mesh per hour
	Solids, % (at 5 hr.)	Lb./hr. (at 5 hr.)			
5.75	3.1	450	0.42	0.78	0.53
11.5	3.9	1500	0.20	0.23	0.86
14.5	3.6	2425	0.17	0.15	1.15

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AN ACCURATE MOUNT FOR TRI-METROGON PHOTOGRAPHY[1]

By R. A. Nodwell[2] and R. C. Burstow[3]

Abstract

A tri-camera mount that fits into the nose of a Mitchell B-25 aircraft and that accurately maintains the interaxial relation between the cameras is described. The alterations and adjustments of the Fairchild K-17 cameras to give the necessary accuracy and interchangeability are also described. Apparent inaccuracies in the mount are discussed, and it is concluded that the main source of error is the instability of the photographic film, which may lead to angular errors of 12 min.

Introduction

In the Canadian method of tri-metrogon tilt analysis outlined by Carroll (2) great saving in time and labour can be effected if the cameras are held rigidly in such a way that the following relations are true:—

(*a*) The optical axes of the three cameras are parallel to a plane, usually vertical;

(*b*) The line joining the transverse fiducial marks in each camera are parallel to the same plane;

(*c*) The interlocking angles between the optical axes of the vertical and oblique cameras are reliably known.

The design and construction of a rigid tri-camera mount that would maintain these relations was undertaken by the Optics Section of the National Research Laboratories, Ottawa, at the request of the Canadian Photographic Research Committee. The mount was to be installed in a Mitchell B-25 aircraft and carry three Fairchild K-17 cameras with Bausch & Lomb 6 in. metrogon lenses. It was specified that the plane defined in each of the cameras by the principal axis and the line joining the fiducial marks transverse to the line of flight be parallel to similar planes in the other two cameras within two minutes of arc. The angles between the principal axis of the vertical camera and those of the oblique cameras were to be approximately 60° with the angles known within three minutes of arc. It was also requested that all cameras be made interchangeable, if practicable, to reduce the seriousness of a breakdown in any one of the cameras by making possible the immediate substitution of a spare.

Alterations to the Cameras

In order to eliminate any possibility of inaccuracy because of movement between the magazine, which carries the fiducial marks, and the camera body the fiducial marks were mounted on the camera body. This is accomplished

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[2] *Physicist.*

[3] *Technical Officer.*

by mounting a plate permanently on the back of the camera (see Fig. 1). This plate duplicates the original camera back except for a raised shoulder $\frac{3}{16}$ in. high, which projects inside the picture frame of the magazine so that the suction back presses on the shoulder when the magazine is in the cocked position. The fiducial marks are mounted on this shoulder. The shoulder reduces the picture size to $8\frac{3}{8}$ by $8\frac{1}{2}$ in., but it was felt by those responsible for the photogrammetry that this disadvantage was compensated for by the added certainty in determining the position of the principal point.

To simplify the procedure in calibrating survey cameras it is desirable to open and close the shutter without disassembling the camera. Unfortunately, no provision is made for this in the K-17 camera. This deficiency is overcome by cutting a slot in the end of the wind gear shaft. The shutter may then be opened or closed by removing the taper pin that locks the wind gear to the shaft and turning the shaft by means of a screwdriver.

Since a dark slide cannot be inserted when the magazine is mounted on the camera, a method was devised to make the magazine light tight while it is being removed from the camera. This is done by replacing the magazine cover locking knob by one of larger diameter and tapping this new knob to take a threaded shaft. The latter shaft, when screwed down, pushes the suction back on to the lip of the magazine. Tests have shown that this makes the magazine light tight. Since the action lifts the magazine slightly the release of the magazine catches must be the first operation performed when removing the magazines. A handle was put on each end of the magazine to facilitate handling.

The Mount

The Mount

The camera mount is a welded joint construction of 1 in. diameter steel tubing reinforced with No. 14 gauge sheet metal. To suit the aircraft the width of the mount had to be kept to a minimum and hence the oblique cameras are located above the vertical one. A completed mount with the cameras is shown in Fig. 2. The mount is insulated from the vibration of the aircraft according to the general method proposed by Reid (4). It is supported on 300 sq. in. of 2 in. thick sponge rubber (medium Dunlopillo) at the plane containing the centre of gravity of the whole assembly. In operation the loading of the rubber is approximately 1 lb. per sq. in.

The details of the method of holding the cameras in the mount are shown in Fig. 3, which is a view from inside the mount. The trunnion *A* has been removed from the camera (not shown) for purposes of illustration. Rotation of the trunnion *A* about the pin *B* permits adjustment of the principal axes of the cameras into parallel planes. The yoke *C* is reamed to fit accurately the shoulder of the screw *D*, which also fits a counterbored hole in the knee *E*. Rotation of the yoke about the screw *D* permits adjustment of the fiducial marks into the correct planes. One of the yokes *C* for each camera has a slot, instead of a reamed hole, which accurately fits screw *D* and allows some motion in the fore and aft direction to accommodate variations in

PLATE I

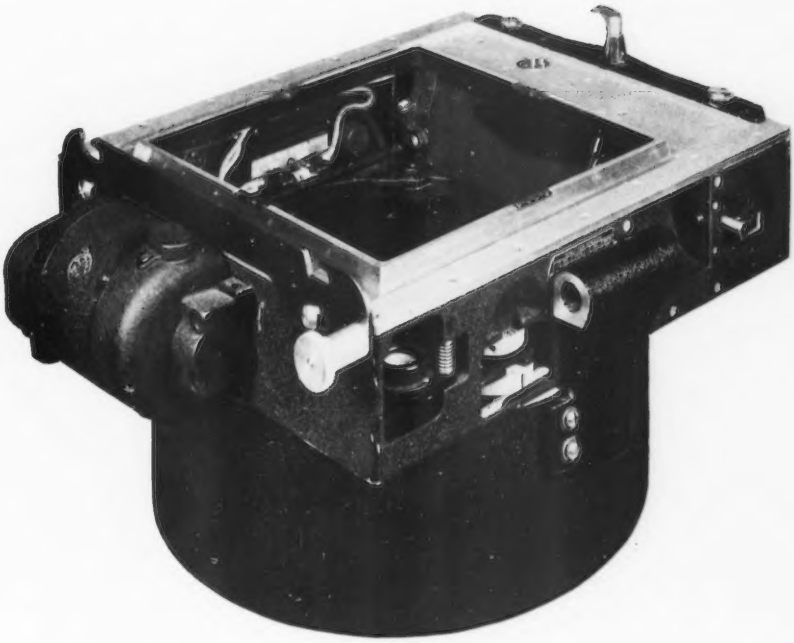

FIG. 1. *A modified K-17 camera.*

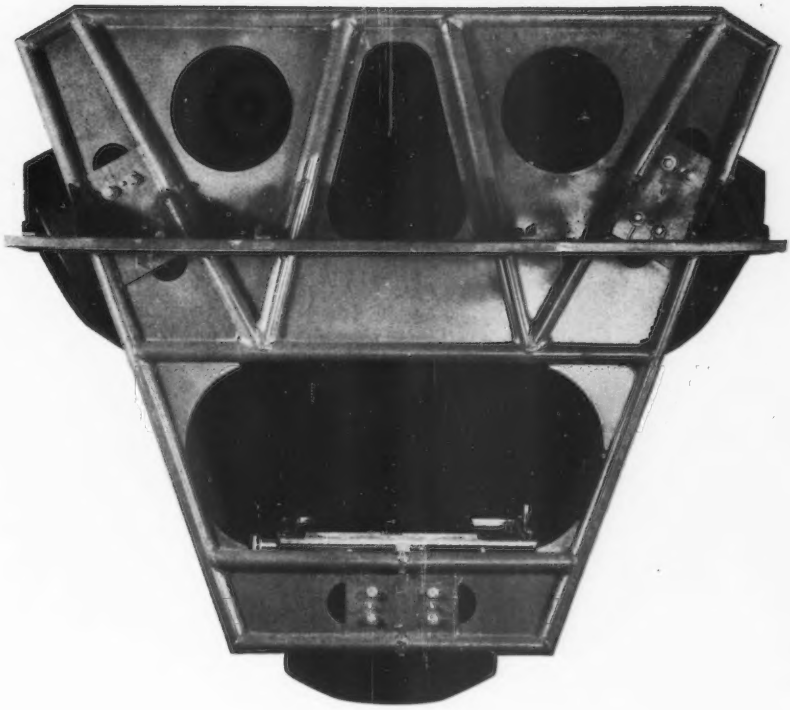

FIG. 2. *The mount.*

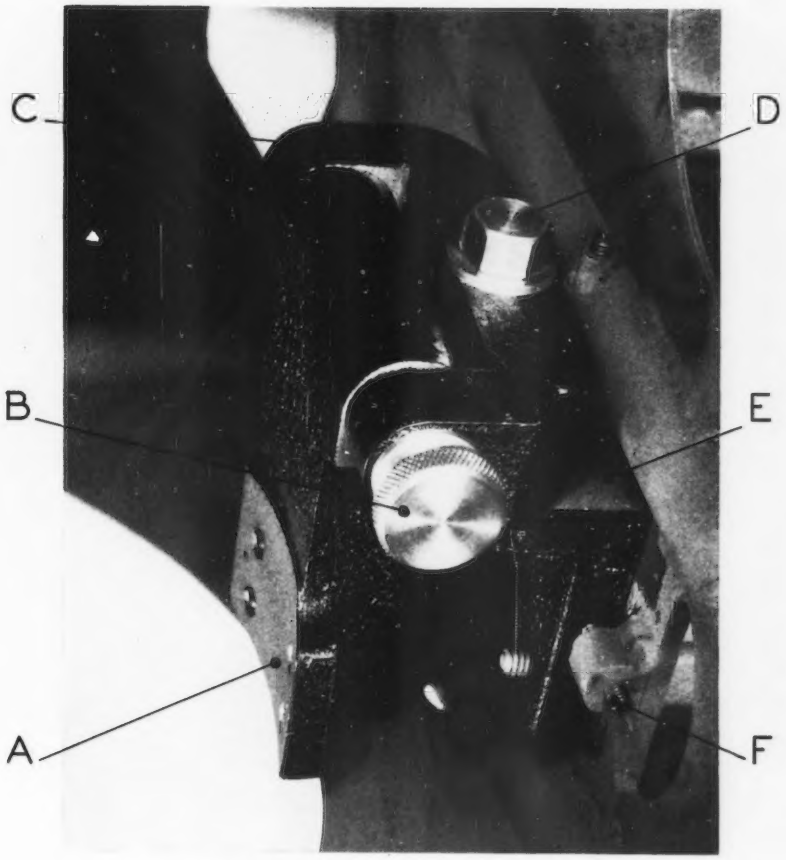

FIG. 3. *The method of positioning the camera in the mount.*

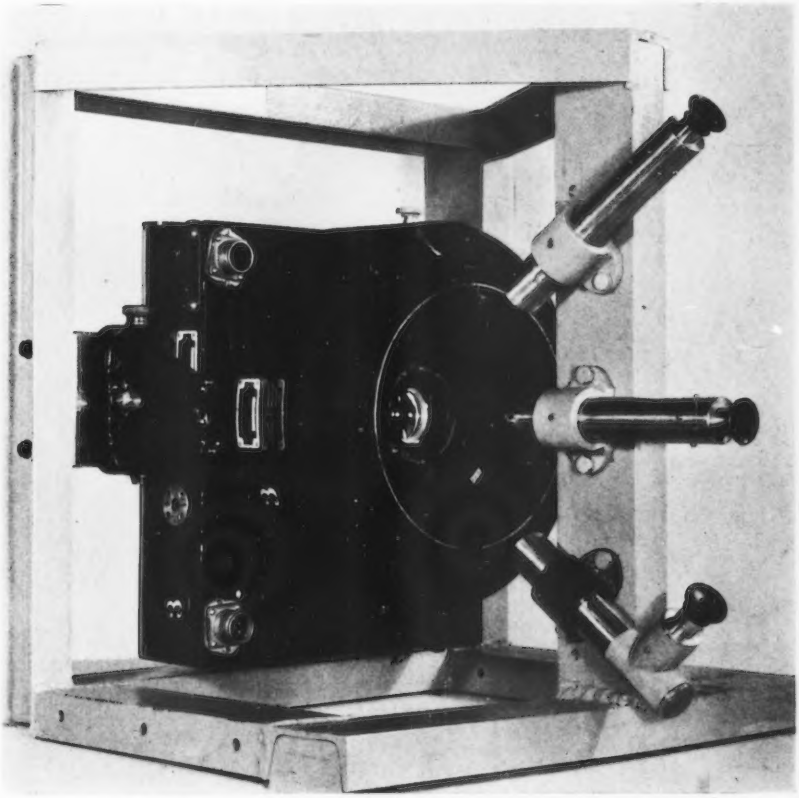

FIG. 4. *The optical jig for locating the camera trunnions.*

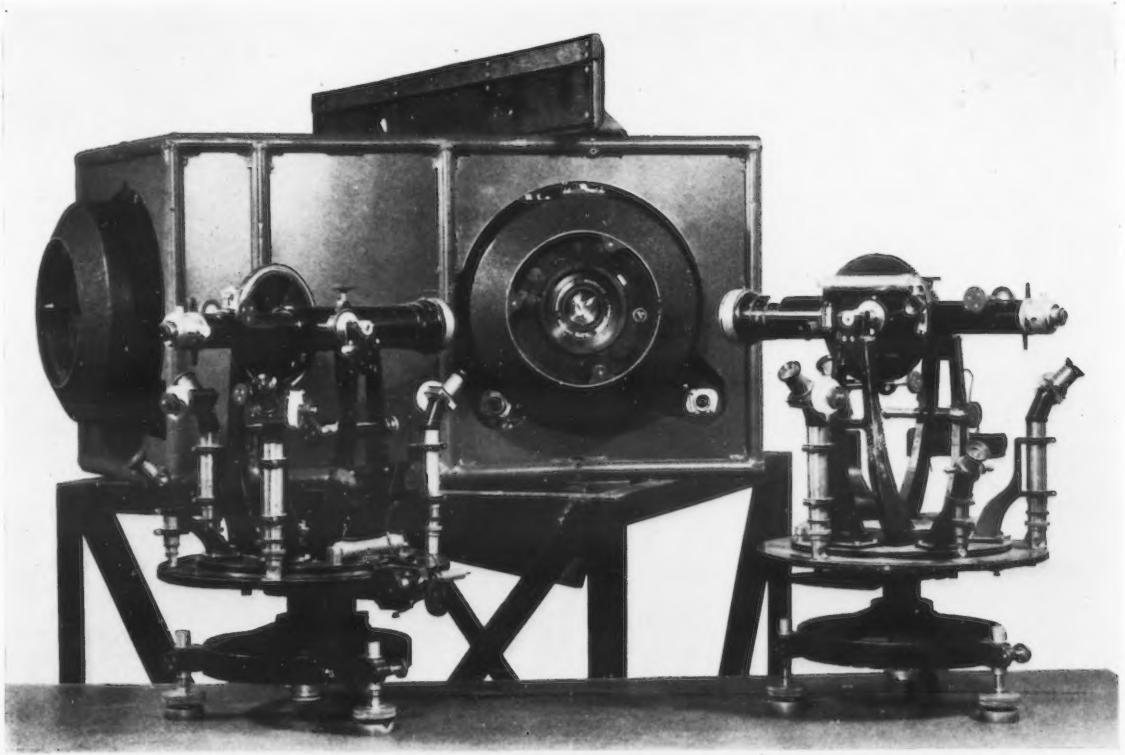

FIG. 5. *The method of adjusting the mount.*

camera diameters. The knee *E* can be moved in two directions by means of opposing screws *F*. All surfaces are machined to tolerances necessary for snug fits and interchangeability.

Method of Adjustment

The location of the principal point and measurement of principal distance of each camera is done by the method outlined by Field (3).

The location of the trunnions of each of the cameras relative to the fiducial marks is accurately established by means o the optical jig shown in Fig. 4. A camera, with its principal point defined by a graticule, is mounted in the rigidly located yokes, and the three telescopes are lined up on the principal point and the two transverse fiducial marks. The first camera is removed, a second camera inserted and shifted on its trunnions until the fiducial marks and principal point line up with the telescopes. When this condition is obtained the trunnions are locked with taper pins. All the cameras are adjusted in this manner and hence are interchangeable.

The method of adjusting the cameras in the mount is as follows (see Fig. 5):--

The mount is placed on its side on top of a welded iron table. The three cameras, each with a graticule defining its principal point, are mounted in position. Two transits are set up to look at the transverse fiducial marks of one camera and levelled. The camera is adjusted by means of the opposing screws (*F*, Fig. 3) until the fiducial marks coincide with the cross hairs of the telescopes. The transits are then moved to the next camera and the process repeated and so on until the plane defined by the transverse fiducial marks of each of the cameras is horizontal. When these planes have thus been made parallel the trunnion knees (*E*, Fig. 3) are locked with taper pins. The angles between the principal axis of the vertical cameras and those of the oblique cameras are measured with the transits.

Performance of the Mount

Three mounts were constructed and installed in aircraft and were used in the summer survey of 1945. The interlocking angles found from the photographs did not agree with the calibrated angles. Typical results from test photographs are shown in the graph of Fig. 6, in which the abscissa is the picture number taken at 5-sec. intervals and the ordinate is the indicated angle between the vertical and the oblique camera. The calibrated angle for the left oblique was 60° 37′ and for the right oblique, 60° 39′. It will be noted that errors up to 12 min. are found in the angle.

The sources of error that might account for this discrepancy and that have therefore been investigated in detail are:—

1. Mechanical instability of the mount,
2. Thermal instability of the mount,
3. Lack of synchronization of the shutters,
4. Instability of the film base.

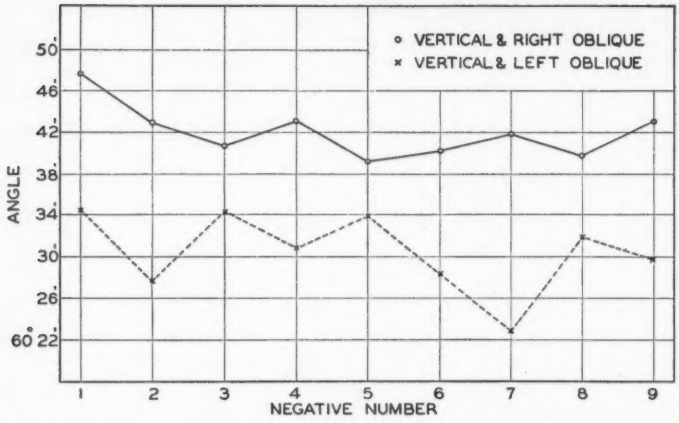

FIG. 6. *Variation in the angle calculated from photographs taken at five-second intervals. The calibrated angle for the left oblique was 60° 37′, and for the right oblique was 60° 39′.*

Mechanical and Thermal Stability

The mechanical and thermal stabilities of the mount were checked in the laboratory. The design calculations, which had indicated that the mount would be adequately rigid, were corroborated. No change in calibration was noted for a temperature change of 60° F.

Shutter Synchronization

A test of the synchronization of the shutters showed that the maximum time lag between any two of the cameras tested was 10 milliseconds. Under the most adverse conditions of aircraft roll this could lead to an error of three minutes.

Instability of the Film Base

The method of calculating the interlocking angle from the photographs will be made clear by a reference to Fig. 7, in which O is the perspective centre and OA and OB the optical axis of the vertical and oblique cameras, respectively. The lines AM_v and BM_o represent the traces of the focal planes, A and B the principal points, and M_v and M_o the fiducial marks of their respective cameras. Conjugate image points lying on or near the line joining the transverse fiducial marks are represented as C_v and C_o. The interlocking angle may be calculated by the formula

$$\theta_v = \tan^{-1} \frac{AC_v}{OA}$$

$$\theta_o = \tan^{-1} \frac{BC_o}{OB}$$

$$\theta = \theta_v + \theta_o$$

These formulae would be accurate for measurements on plate but, normally, distances measured on film are inaccurate owing to change in dimension of

the film base following processing (1). To compensate for this factor the fiducial distance (the distance from fiducial mark to principal point) had been measured on photographic plate for each of the cameras. The distance from the fiducial mark to the image point (M_vC_v) was measured and subtracted

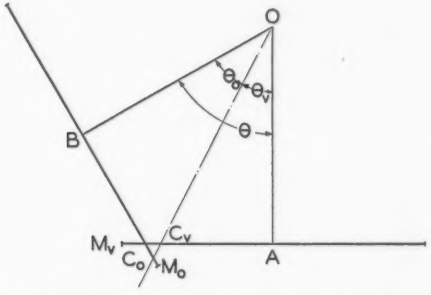

FIG. 7. *The geometrical relation between the cameras.*

from the fiducial distance to give a corrected value of the distance AC_v. Although M_vC_v is measured on film it is always short (2.8 cm. maximum), so the shrink correction is assumed to be negligible. This assumption was checked in several cases by measuring the apparent fiducial distance on the film and multiplying M_vC_v by the ratio of this apparent fiducial distance to the true fiducial distance. In no case had the assumption introduced an error greater than 3/10 min.

All measurements were made with a comparator that reads directly to 0.002 mm. For objects not at infinity, correction to the computed angle was made to allow for non-coincidence of the camera lenses.

On pictures taken directly over the city where much sharp detail was available several pairs of conjugate points were identified and the interlocking angle calculated for each pair. The results for several photographs are shown in Fig. 8. The abscissa is the distance of the image point from the fiducial mark of one of the cameras. These graphs indicate that even after allowance has been made for over-all changes in the film large errors can occur owing to local distortions.

The cause of this local film distortion has not been investigated, but it has been suggested that it may be caused by water drops drying very quickly and shifting the emulsion.

Although the errors found in local film shrink were large enough to account for the discrepancy between the calibrated and apparent angles of the mount, it was felt that a positive check on the calibration was desirable. Hence the mount was set up in the laboratory and pictures were taken on both plates and films. The graph of Fig. 9 shows the angle obtained on plates and on two

consecutive pictures taken on the rolls of films. The results from plates check very well with the calibrated angle of 60° 30.5′, but although the film was processed carefully by hand, some discrepancy is still indicated, especially in the first picture.

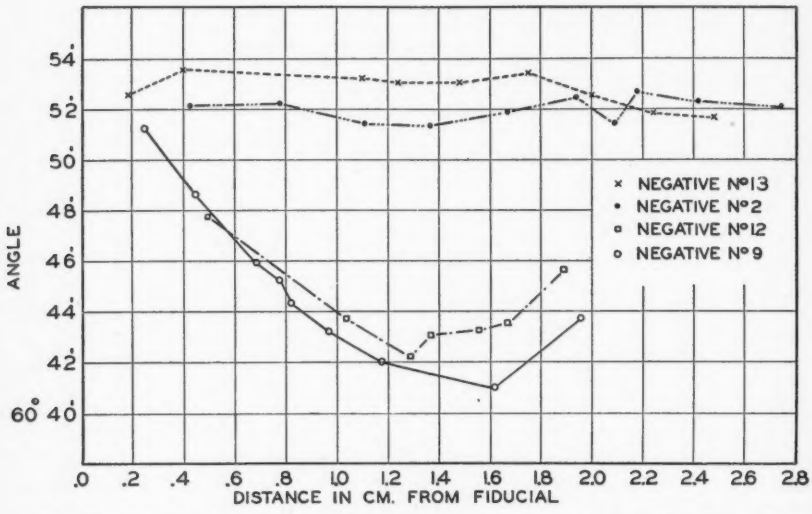

FIG. 8. *Variation in the calculated interlocking angle due to local film distortion. The angle is between the vertical and the right oblique cameras.*

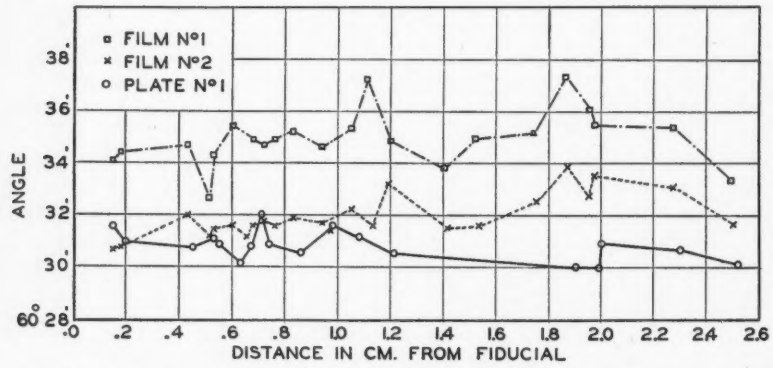

FIG. 9. *Comparison of photographs on plate and film. The angle is between the right oblique and vertical cameras. This angle was calibrated at 60° 30.5′.*

The sudden small changes on all of these graphs could be repeated but it is felt that this is due to the fact that the precision of measuring is greater than the accuracy of identifying conjugate points and that they are therefore not significant.

The effect of temperature rise due to heat from the illuminating lamp is an interesting illustration of the care necessary in making accurate measurements of photographic film. This effect is illustrated in the graph of Fig. 10. In

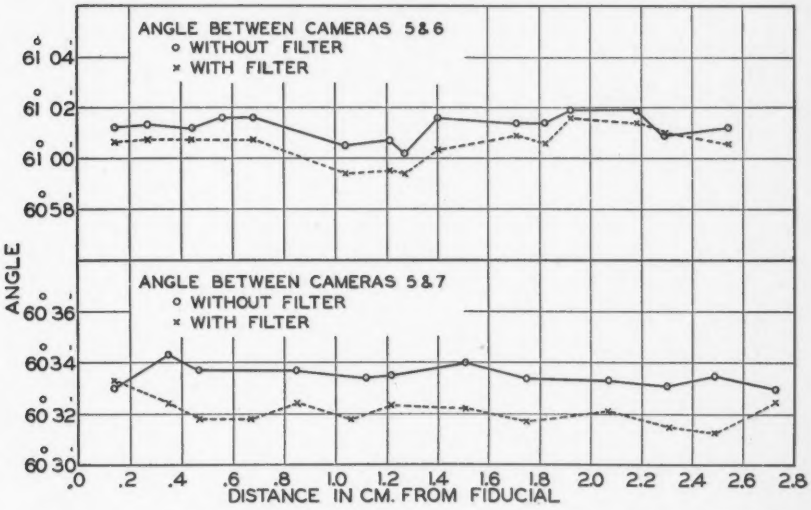

FIG. 10. *Temperature effect on film. Camera No. 5 is vertical, No. 6 right, and No. 7 left.*

the first curve, readings were taken with illumination falling directly on the film; in the second, heat absorbing filters were mounted between the lamp and the film. The change in angle is quite definite although the rise in temperature due to the lamp was not more than 15° F.

Conclusion

The tri-camera mount is mechanically rigid, but the lack of synchronization of the shutters may lead to errors as high as three minutes. The greatest source of error in using tri-metrogon methods is in local film distortion, which can lead to errors of 12 min. When paper prints are used this error will probably be greatly increased.

Acknowledgments

It is desired to acknowledge the wholehearted co-operation of W/C H. Pearce of the Directorate of Photography, R.C.A.F. Headquarters, and the personnel of No. 7 Photographic Wing, Rockcliffe Air Station. Their assistance was particularly valuable whenever compromises had to be made between service and experimental requirements. All modifications to the aircraft were devised and carried out by No. 7 Photographic Wing.

The authors wish to express their appreciation to Dr. L. E. Howlett for his advice and assistance in this project.

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DIMENSIONAL CHANGES IN SAFETY TOPOGRAPHIC AERO FILM UNDER SERVICE CONDITIONS[1]

By P. D. Carman[2]

Abstract

A study has been made of the dimensional changes in Eastman Super XX Aero Topographic Safety film exposed in routine survey operations. Scale error varies from + 0.02% to + 0.45%, distortion from − 0.11% to + 0.08%. The largest errors are due to variations in the temperature and humidity to which the film is subjected. Control of these is recommended. Smaller errors indicate need for improvements in film base and need for a better film squeegee before the drier.

Introduction

Papers dealing with dimensional changes occurring in photographic film have been published by Calhoun (1), Clark (3), Davis and Stovall (4), Eastman Kodak (5), and Tupper and Clark (7, pp. 208-225). Only that by Calhoun gives information on the behaviour of film in normal use as well as under laboratory conditions. Unfortunately it deals only with motion picture film, not survey film. Some unpublished data on aerial film have been made available to the author (2).* These data again deal with dimensional changes measured under laboratory conditions.

It is the purpose of the present study to provide general information on the dimensional changes likely to be encountered in survey operation, with a view to determining what accuracy is now available to the photogrammetrist and to ascertaining what improvement is possible by acceptable revisions of service procedure. In this study, the only departure from routine conditions is the measuring of the film under constant humidity and constant temperature. This is necessary to any attempt at interpretation of the changes. The further errors which would have arisen from random ambient conditions can be estimated readily.

Experimental Procedure

Measurements were made on films that had been exposed in regular R.C.A.F. tri-camera survey operations. The K-17B cameras used had previously been modified by the National Research Laboratories to make them suitable for accurate survey photography (6). One of the modifications had been the provision of fiducial marks attached to the camera body. These fiducial marks were designed so that the distances between certain edges of opposite pairs would provide accurate reference dimensions. To obtain these fiducial distances initially a photographic plate placed in the film plane of the

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Contribution from the Division of Physics and Electrical Engineering, National Research Laboratories, Ottawa, Canada. Issued as N.R.C. No. 1452.

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* *And secret reports of the British Ministry of Aircraft Production.*

camera was exposed to light coming through the camera lens. The distances between the fiducial mark images so produced were then measured. All were approximately 8 in. (200 mm.).

Six rolls of film were studied. They consisted of two groups, T49 and T50, each containing the concurrently exposed rolls, *L*, *C*, and *R* (left, centre, and right). Measurements of the fiducial distances were made on groups of four negatives at each of four positions in the roll. These positions were at the beginning of the roll, at the end of the roll, and two intermediate positions. One of the two intermediate positions was chosen to fall at the beginning of a flight line. The other was remote from the ends of any flight line. In addition, a set of measurements was made at frequent intervals throughout the entire length of one roll. Results of the first series of measurements are given in Fig. 1. Results of the second series of measurements are given in

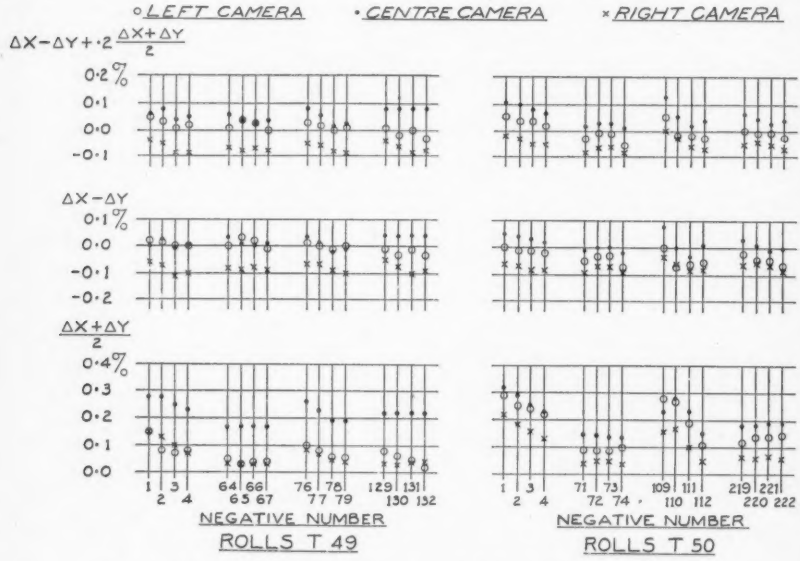

FIG. 1. *Scale change and distortion on selected negatives from six rolls.*

Fig. 2. The *X* direction has been taken parallel to the length of the film, the *Y* direction is at right angles to it. A positive value of $\triangle X$ or $\triangle Y$ indicates enlargement or 'stretch' of the film between exposure and measurement.

Accuracy

The films were measured at 64% relative humidity and 70° F. For the first type of measurement, each group of four negatives was left unrolled under these conditions for 48 hr. To ascertain the accuracy being obtained, a considerable number of measurements were completely repeated after intervals

of up to three weeks. The maximum spread of values obtained was 0.02%. Most discrepancies were 0.01% or less. Hence the values given are correct to within ±0.01%.

For the second type of measurement it was impracticable for each negative to be conditioned unrolled. However, at the time these measurements were made the roll had been in the constant humidity, constant temperature room for about two months and had been wound through several times. There are no indications that the resulting accuracy is significantly worse than that obtained in the other type of measurement.

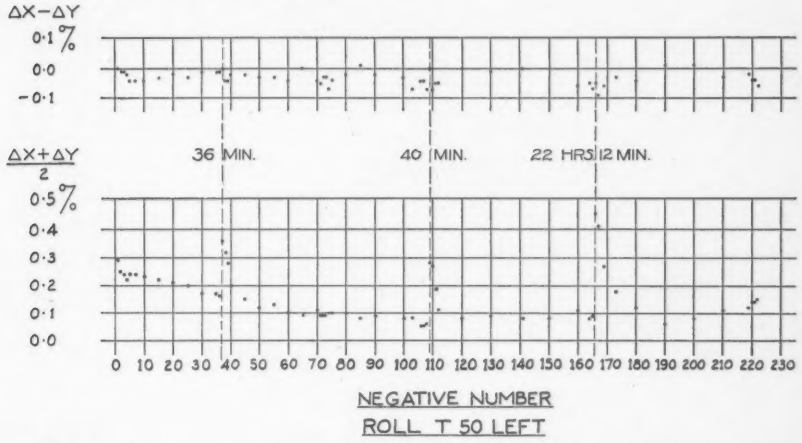

FIG. 2. *Scale change and distortion throughout one roll. Broken lines indicate beginning of flight lines after intervals shown.*

Related Data

Certain subsidiary data are required to permit an analysis of the results obtained.

Owing to the fact that the films were exposed under service conditions, only data regularly recorded are available. The relevant portion is given in Table I.

To obtain information on the film temperatures to be expected, a flight was made with thermocouples installed inside the magazines. At 20,000 ft. with an outside air temperature of −15° C. and with no heat turned on in the camera location, magazine temperatures were: left, 14° C.; centre, 9° C.; right, 14° C. The 'greenhouse' effect is very pronounced at the camera position in the nose of a B25 aircraft. The centre camera is lower than the obliques and shaded by the mount.

It is also necessary to have certain approximate data on the physical properties of the film—Eastman Kodak Topographic Safety. Measurements of the coefficient of linear expansion with temperature obtained by an English worker* are given in Table II.

* *Secret reports of the British Ministry of Aircraft Production.*

TABLE I

EXPOSURE DATA

Roll	Emulsion	Neg. No.	Time photos taken	Date 1945	Altitude, ft.	Magazines	Outside air temp. at altitude, °C.	Outside air temp. at take-off, °C.	Take-off time
T49	55-343-3	1–46	1045–1106	13 April	19,900	*A*	−26	+ 5	0916
		47–75	1010–1024	16 April	19,672	*A*	−19	+ 6	0900
		76–103	1042–1059	16 April	19,672	*A*	−19	+ 6	0900
		104–132	1027–1041	1 May	19,025	*A*	−12	+10	0930
T50	55-343-8	1–36	1110–1124	1 May	19,025	*C*	−12	+10	0930
		37–108	1200–1225	1 May	19,025	*C*	−12	+10	0930
		109–165	1305–1330	1 May	19,025	*C*	−12	+10	0930
		166–222	1142–1204	2 May	18,844	*C*	− 9	+12	—

TABLE II

Type of film	Coefficient of linear thermal expansion	
	X, along film	*Y*, across film
American type 1A, Class L, topographic base	72×10^{-6}	104×10^{-6}
Kodak topographic acetate base made in America and coated at Harrow, England	61×10^{-6}	71×10^{-6}

Coefficients are for a relative humidity of 75% and are per degree centigrade.

Adequate information on change of length with change of humidity for this type of film could not be found in the literature. Hence sufficient work was done to obtain an indication of this effect. Film conditioned at 64% relative humidity and 70° F. was transferred to a desiccated chamber at the same temperature. Measurements of shrink were made over a long period following the transfer. Results are presented in Fig. 3. The film used was Eastman Kodak Topographic Safety but it was not from the survey rolls studied.

Discussion

$$\text{Scale error } \left\{\frac{\triangle X + \triangle Y}{2}\right\} \text{ ranges from } + 0.02\% \text{ to } + 0.45\%$$

$$\text{Distortion } (\triangle X - \triangle Y) \text{ ranges from } - 0.11\% \text{ to } + 0.08\%$$

Scale Error

With regard to scale error, a prominent effect is the transient increase at the beginning of each flight line (see Fig. 2). This can be attributed to the fact that these negatives had time before exposure to become conditioned to the humidity and temperature existing in the cameras. The minimum interval

between lines is 18 min. During this interval the position of the film in a magazine is as follows. The negative next to be exposed is in position in the focal plane. The one to follow it is partly (4 in.) in transit over the feed guide and roller, partly ($4\frac{1}{2}$ in.) on the outside of the supply spool. The

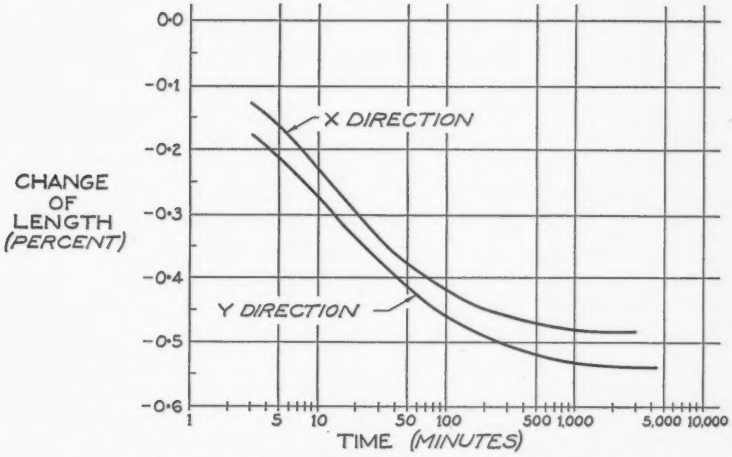

FIG. 3. *Conditioning shrink on transfer from 64% relative humidity, 70° F., to a desiccated chamber at the same temperature.*

third one is partly ($7\frac{1}{8}$ in.) on the outside of the supply spool and partly ($1\frac{3}{8}$ in.) on the second layer. The fourth one is entirely on the second layer of the supply spool. (Dimensions are for supply spool half-full.) The observed scale change decreases in magnitude in the above order, which is the order of degree of exposure to conditioning. (It might appear that the second negative is exposed equally to the first. However, the second is inside the magazine where the dryness of the air will be affected by the mass of film present.)

Fig. 2 clearly shows the gradual increase in scale change that occurs toward the beginning of each roll. This increase may be attributed to the gradual conditioning of the entire roll from the outside inward. The initial peak is missing here because a few test exposures were made shortly before the beginning of the flight line.

It is interesting to note that the peak at T50L 166, which is much higher than the other two, corresponds to a much longer conditioning line.

The conditioning could be to low humidity or low temperature. It is indicated that the film temperature would be between 0° and 20° C. as compared with the 21° C. at measurement. For an average coefficient of 77×10^{-6}, 20° C. would produce a scale change of only 0.15%. This maximum value is insufficient to account for the observed changes.

The temperature difference between the outside air and the camera compartment would result in a very low relative humidity. (For an outside humidity of 50%, an outside temperature of −15° C., and an inside temperature of 12° C., the inside humidity would be 6.6%.) Hence it can be seen from the data of Fig. 3 that this alone could account for almost the entire scale change.

The two effects combined account for the observed changes.

A few further points in connection with a scale change are worthy of note. There is a suggestion of an increase in scale change toward the end of the T50 rolls. This could be attributed solely to temperature conditioning working out from the metal core. Humidity conditioning might also contribute to the effect. It would not be present in the T49 rolls since they were not used to the end. The generally positive value of scale change can be attributed to two causes. The measuring humidity is somewhat higher than the humidity in which the film was spooled by the manufacturer (by about 4%, corresponding to a scale change of 0.03%). A slight conditioning takes place before exposure even with the 30 sec. picture interval.

Permanent shrink has been neglected in the above discussion. It is known to be small during processing, and is probably not large for topographic base even over the 10 month interval between exposure and measurement. Correction for any present would tend to shift the scale change plots upwards somewhat without invalidation of any of the explanation.

Differences between negatives exposed simultaneously in different cameras are not clearly explicable. Possible causes are discussed later.

Distortion

Distortion effects cannot be accounted for as satisfactorily as scale changes. One would expect $\triangle Y$ to be 10 to 40% larger than $\triangle X$ (1).* Thus $\triangle X - \triangle Y$ would be equal to $\frac{\triangle X + \triangle Y}{2}$ times a constant between −0.10 and −0.33. From Fig. 1, the *average* scale change is 0.139% and the *average* distortion −0.028%. These figures bear a ratio of 1 to −0.20, which is in the above range.

However the ratio varies widely with individual negatives, from −3.0 to +1.0. A plot of this ratio would tend to be misleading since large changes in ratio arise from small changes in distortion on negatives for which the scale error is small. Instead the top graph of Fig. 1 is a plot of the measured distortion minus the distortion that would have occurred if the ratio −0.20 had been uniformly effective. This graph demonstrates that the average value of the distortion is without much significance since correction for it makes little difference in the distortion range.

Probable Causes of Remaining Errors

Because the observed errors result from conditions that at present are neither controlled nor measured in service no rigorous explanations can be

**And secret reports of the British Ministry of Aircraft Production.*

established for some of them. This is not completely satisfactory from an academic point of view, but is of little practical significance compared to the current value to photogrammetry of the information obtained in the test. Although rigorous explanations are not always possible, plausible ones can be advanced for the remaining errors.

Most apparent of these errors are the persistent differences between rolls that appear both on scale error and distortion (Fig. 1). For each negative number the value for the centre camera is distinctly greater than that for the right camera, with average differences of 0.10 and 0.08% on distortion and 0.16 and 0.11% on scale change for T49 and T50 respectively. Values for the left camera are more random. They usually lie somewhere between the other two. Yet for T49, left camera values are close to those of the right camera on scale error, and close to those of the centre camera on distortion, while, for T50, left camera values are generally intermediate.

This effect could be due either to variation in exposure conditions or to variations in the properties of the film. The latter explanation requires a somewhat fortuitous repetition in the loading of the centre and right magazines. The chances of such a repetition are not unduly low and might have been increased by systematic film handling. This explanation would account for the differences between T49 left and T50 left. Properties of the film that might vary to produce the effect are coefficients of linear expansion with temperature, dimensional changes due to processing, and dimensional changes during storage. One case of variation in temperature coefficient has been found by an English worker while investigating a different aspect of film behaviour (see Table II). For exposure at 0° C. variations of the size he found would account for almost half the average difference between films exposed in the centre and the right cameras.

Variation in exposure conditions seems unlikely to have caused the effect. This is seen from the following consideration of the various possible causes.

1. The centre camera, which is indicated to be the coldest, shows the biggest scale change. However, its lower temperature would produce an increase in relative humidity slightly more than sufficient to nullify the thermal contraction. There remains the remote possibility that the relative humidity was so low as not to be affected significantly by the temperature difference. Even admitting this, the observed temperature difference of 5° C. produces a scale change of only 0.04%, which is ½ to 1/5 the observed range. Thus there is little possibility of temperature variation causing the scale change differences and no apparent means whereby it could cause the distortion differences.
2. Relative humidity differences arising from ventilation variation are another possible cause of the scale error differences. However, the initial rate of conditioning—about 0.15% in three minutes—from Fig. 3 is not sufficient to explain the differences. Effective conditioning time could hardly be more than 90 sec. except at the beginning of a run. The humidity differences between cameras could not be great or the effects

of conditioning on the first few pictures of a line would differ markedly. Relative humidity, like temperature, cannot explain the distortion differences.

3. Errors in the positioning of the film relative to the fiducial marks are unlikely since the cameras were checked for this after modification. Clearance between the fiducial marks and the film was nominally 0.003 in. All clearances were kept under 0.005 in.

4. Overexposure of the fiducial mark images in the sky portion of the obliques might contribute toward the persistent distortion differences but would not be sufficient to provide for the approximately 0.2 mm. (0.1%) required.

   To demonstrate this, a 1 mm. slit was contact printed on Aero Super XX film with a wide range of exposures. Development was a laboratory duplication of that used in service. For resulting densities between 0.8 and 1.6 the variation in image width was less than 0.005 mm. Even for a density range from 0.4 to 3.0 the variation in image width was only 0.060 mm.

5. Mechanical tension on the film may also be considered. The greatest tension would occur when the film in the focal plane shrank from conditioning effects while the pressure back was down and the suction on. To duplicate the suction conditions which were not accurately known, tests were made in an aircraft in flight. It was found that a force of 30 lb. was required to pull film through the magazine with the back down and suction on. (The suction, measured in the line at a point 6 ft. from the magazine, was $1\frac{5}{8}$ in. of mercury below the surrounding atmospheric pressure.) Hence the forces arising due to contraction of the film would produce an elastic stretch of only 0.03% (2).

Thus there seems little likelihood that exposure conditions alone can have produced the differences between rolls exposed simultaneously. Hence it seems probable that these differences are due primarily to variations in the properties of the film.

Random Errors

Allowing for the various forms of persistent errors that have been discussed, it is apparent that random errors remain. The maximum values of these are of the order of $\pm 0.03\%$ on scale and $\pm 0.05\%$ on distortion. (As is to be expected statistically, the latter is about twice the former.) These random errors are of the same order as those found by other workers in the measurement of distortion arising in processing. Hence there is no reason to attribute them to any other cause.

It should be noted that there is no evidence for treating these random errors as percentage errors. They are more likely to be linear displacements independent of the distance over which the measurements are made (6). Small water drops on the film as it enters the drier are a probable cause.

Conclusions and Recommendations

Scale error $\left\{\frac{\Delta X + \Delta Y}{2}\right\}$ ranges from $+ 0.02\%$ to $+ 0.45\%$.

Distortion $(\Delta X - \Delta Y)$ ranges from $- 0.11\%$ to $+ 0.08\%$.

Scale change is not an extremely serious difficulty to photogrammetrists, provided it is known, since corrections can be applied. However, if it is not determined for every negative, errors up to 0.4% may arise since scale varies considerably throughout a roll. This variation can be reduced to less than 0.1% by maintaining the film at spooling temperature and humidity prior to and during exposure. Such a procedure is recommended. Since its introduction will take considerable time the following three interim measures are suggested. (1) Obtaining the film from the manufacturer in humidity sealed tins would provide easy maintenance of humidity conditioning up to the moment of loading. (2) The cameras should be maintained at 70° F. to avoid temperature effects. (3) The cameras should be started several exposures before the beginning of each line so that the first few negatives may be discarded. For intervals of about half an hour between lines, five such preliminary exposures are sufficient. For a 24 hr. interval the number should be about 15.

For the above measures to be fully effective, the film should be reconditioned to spooling temperature and humidity for printing.

Distortion is much more serious to the photogrammetrist than scale change since he has no convenient method of correcting for it. The measures recommended for reducing scale error may also reduce distortion somewhat, but the distortion problem is largely one for the film manufacturer.

Random errors cause a total variation of 0.06% on scale, 0.10% on distortion. To reduce these it is recommended that a highly efficient squeegee be installed on the processing machine between the washing tank and the drier.

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TECHNOLOGY

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